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LXI. *On the Passage of Light Through Transparent Plates.*
By Sir ARTHUR SCHUSTER, D.Sc., F.R.S.*

[Plate XII.]

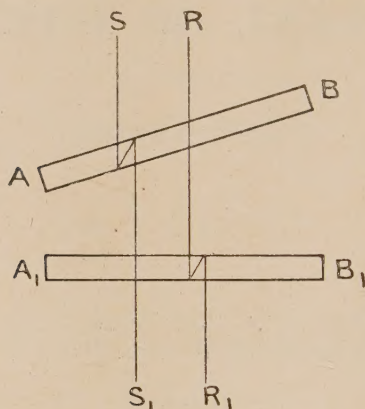
IN explaining the optical effects observed under suitable conditions in light that has passed through transparent plates, it is the present practice to select certain groups of rays and to apply the principle of interference. I propose to substitute a more rational procedure which discards the conception of rays and seeks guidance by following the wave-fronts. It is my object to show that this method is more general and more effective. As an illustration I take the so-called interference effects observed in parallel light after its passage through two mutually-inclined transparent plates, Brewster's bands being a special case of the general problem. Owing to the inclination of the plates, backward and forward reflexions *between* the plates need not be taken into account.

The current method is to select two rays RR_1 and SS_1 (fig. 1) of which the former has passed through the first plate (AB) and been twice internally reflected in the second (A_1B_1), while the latter has suffered two internal reflexions

* Communicated by the Author.

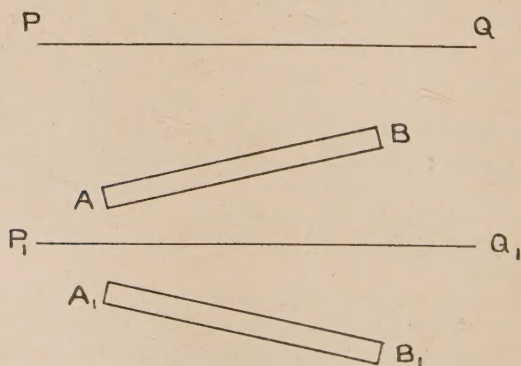
in AB and passed straight through A_1B_1 . A slight difference in path due to an inclination of one of the plates or a difference in thickness will cause a change of the combined amplitudes by so-called interference. The complete solution requires a lengthy calculation, rays that have been internally reflected more than twice being taken into account.

Fig. 1.



If, on the contrary, we consider not rays but wave-fronts, the problem presents an altogether different and simpler aspect. The wave-front PQ (fig. 2) having passed

Fig. 2.



through AB and reached a position such as P_1Q_1 , is no further concerned with AB . Its subsequent fate depends entirely on the second plate. If J_1 represents the fraction of the intensity of light that passes through AB and J_2 the

corresponding fraction for A_1B_1 , the intensity transmitted through the combined plates is simply J_1J_2 . There is here no question of interference: we do not add amplitudes, but multiply transmittances.

I shall assume the effects of a single plate to be known. To an eye focussed for infinity, homogeneous light appears as a succession of bright and dark rings, and the greater the reflecting power of the plate, the more will the light be concentrated in the circles of maximum intensity until, in the limit, when the reflecting power is equal to unity, the bright rings are reduced to lines. With two plates, acting independently, each would produce a system of concentric rings. In Pl. XII. the two systems are drawn with P and Q as centres, and the combined effect is obtained by taking the product of the separate intensities. It is apparent that the maxima will be concentrated at the intersection of the circles, and in the limiting case of linear rings the light is entirely confined to a number of points, the position of which is easily calculated. If the centre of each system is a point of maximum intensity, the radii of rings having maximum intensity are in the ratio of the square roots of successive integer numbers. Referred to a system of coordinates in which the line joining the two centres is the axis of x and the origin is at a point half-way between the centres, the rings are represented by the equations

$$y^2 + (x-a)^2 = R^2m; \quad y^2 + (x+a)^2 = R^2n,$$

where m and n are integers and R is a linear constant. Subtracting and adding these equations, we find

$$4ax = R^2(n-m); \quad y^2 + x^2 = \frac{1}{2}R^2(m+n).$$

Hence the points of maximum intensity for equal values of $m-n$ lie on equidistant straight lines parallel to the axis of y and, for equal values of $m+n$, on circles having the origin of coordinates (O) as centre. Pl. XII. shows the lines of maximum intensity in the original system of rings as well as the straight lines and circles having O as centre.

For a complete solution of the distribution of intensities, we must turn to Airy's equation for a single plane parallel plate. To an eye focussed for infinity the intensities are represented by

$$J = \frac{(1-s)^2}{(1+s^2) - 2/s \cos \delta},$$

2 T 2

where s is the coefficient of reflexion at the surface of the plate, and the angle δ is defined by

$$\delta = 4\pi e \cos \gamma / \lambda,$$

γ denoting the angle between the wave normal and the plate normal inside the plate, and λ the wave-length, also measured inside the plate, while e is its thickness. For a combination of two plates we have therefore

$$I = J_1 J_2 = \frac{(1-s_1)^2}{(1+s_1^2)-2s_1 \cos \delta_1} \cdot \frac{(1-s_2)^2}{(1+s_2^2)-2s_2 \cos \delta_2} \quad (1)$$

In the problems which are of practical importance we may assume s_1 and s_2 to have the same value. It is convenient to substitute for δ_1 and δ_2 two other variables ϵ and ζ , such that

$$2\epsilon = \delta_1 + \delta_2; \quad 2\zeta = \delta_1 - \delta_2.$$

Writing

$$I = (1-s)^4 / D,$$

we then find:

$$D = (1-s^2)^2 + 4s^2(\cos^2 \epsilon + \cos^2 \zeta) - 4s(1+s^2) \cos \epsilon \cos \zeta, \quad (2)$$

or if

$$a = 1 + s^2; \quad b = 2s,$$

$$D = (a^2 - b^2) \sin^2 \zeta + (b \cos \epsilon - a \cos \zeta)^2. \quad (3)$$

These equations are perfectly general, but in what follows we shall confine ourselves to two plates of equal thickness.

Let the normals to the two plates be in the plane of xy and form equal angles $\pm \alpha$ with the axis of x . The observing eye E (fig. 3) being in the axis of x , we take a line of sight ES forming an angle ϕ with the axis of x so that the direction cosines of the line of sight are

$$\cos \theta \cos \phi, \quad \cos \theta \sin \phi, \quad \sin \theta.$$

If the angles between the two mirrors be 2α , the line of sight will form angles γ_1 and γ_2 with the normals to the plates, which are determined by

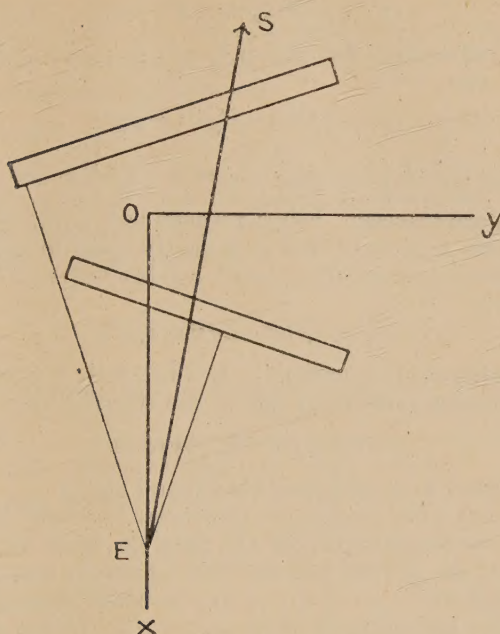
$$\cos \gamma_1 = \cos \theta \cos (\phi - \alpha); \quad \cos \gamma_2 = \cos \theta \cos (\phi + \alpha).$$

If p be the distance of E from the origin, the point at which the line of sight cuts the plane yz is

$$x = p = r \cos \theta \cos \phi, \quad y = r \cos \theta \sin \phi, \quad z = r \sin \theta,$$

the value of r for a given line of sight being determined by the first of these equations.

Fig. 3.



In order to avoid unessential complications, we take the optical medium to be air, as in Fabry and Perot's interferometer, so that the direction of the line of sight is not altered by its entry into the plates. Writing c for e/λ , we then have

$$\left. \begin{aligned} \delta_1 - \delta_2 &= 2\pi c(\cos \gamma_1 - \cos \gamma_2) = 4\pi c y \sin \alpha / r \\ (\delta_1 + \delta_2) &= 2\pi c(\cos \gamma_1 + \cos \gamma_2) = 4\pi c p \cos \alpha / r \end{aligned} \right\} \dots (4)$$

The second of these equations shows that lines drawn in the directions for which $\delta_1 + \delta_2$ has the same value cut the plane yz in circles, the radii (R) of which are determined by the equation after substitution of $p^2 + R^2$ for r^2 . If the line of vision be—as will usually be the case—confined to directions forming small angles with the axis of x , we may in the first equation take approximately r to be equal to p . The locus of the lines in the plane yz for which $\delta_1 - \delta_2$ is constant are straight lines, two successive lines at which $\delta_1 - \delta_2$ differs by 2π being separated by a distance $p/2c \sin \alpha$. Without approximation, and referred to a system of coordinates parallel to the one used above, but passing through the point of observation E (fig. 3), the directions for which $(\delta_1 - \delta_2)$

has constant value lie on the cone

$$(1 - \kappa_1^2)y^2 - \kappa_1^2(x^2 + z^2) = 0, \quad . \quad . \quad . \quad (5)$$

while the directions for which $\delta_1 + \delta_2$ is constant lie on the circular cone

$$(\kappa_2^2 - 1)x^2 + \kappa_2^2(y^2 + z^2) = 0, \quad . \quad . \quad . \quad (6)$$

where

$$\kappa_1 = (\delta_1 - \delta_2)/4\pi c \sin \alpha; \quad \kappa_2 = (\delta_1 + \delta_2)/4\pi c \cos \alpha,$$

κ_1 and κ_2 are fractions, being respectively equal to y/r and p/r , so that κ_1 is small and κ_2 is nearly equal to unity. The first of these cones cuts the plane $x=p$ in a curve, the equation of which is

$$(1 - \kappa_1^2)y^2 - \kappa_1^2z^2 = \kappa_1^2p^2.$$

This represents an hyperbola. If z be small compared with p , the equation reduces to that of the straight lines

$$y = \kappa_1 p = (\delta_1 - \delta_2)p/4\pi c \sin \alpha,$$

in agreement with what has been found above.

The cones which define the directions for which $\delta_1 - \delta_2$ and $\delta_1 + \delta_2$ have constant values are fixed in space for a given position of the optical plates. The equations may therefore be modified, and applied to any directions of vision by determining the intersections of the cones with planes which are at right angles to the required line of vision, or preferably refer the cones to a system of coordinates in which the plane yz is normal to that line.

It is not my object to discuss particular cases, but two obvious conclusions may be mentioned. The lines for which $\delta_1 - \delta_2$ is constant are determined by the cone defined by equation (5), which represents a surface of revolution round the axis y . Revolving this cone round its axis leaves it unchanged, and hence, so long as the point of observation remains in the plane xz , the locus of $\delta_1 - \delta_2$ remains the same. That plane is fixed relatively to the plates. On the other hand, the locus for $\delta_1 + \delta_2$ is a cone of revolution having the axis of z as axis, and we may therefore turn the mirrors round that axis without changing the curves for which $\delta_1 + \delta_2$ has a constant value.

The circles and straight lines shown in Pl. XII. all pass through the points of maximum intensity, but within each line the intensity fluctuates. It is of interest to calculate the average intensity for the loci of constant $\delta_1 - \delta_2$. Equation (1) shows that there is a maximum of intensity when $\cos \delta_1 = \cos \delta_2 = 1$, and a minimum when $\cos \delta_1 = \cos \delta_2 = -1$.

If $\zeta=2m\pi$, we find by the definition of ζ and ϵ that of $\cos \delta_1 = \cos \delta_2$. The lines so defined contain, therefore, both the maxima and the minima according as $\cos \epsilon = \pm 1$. Substituting this value of ζ in equation (3), we find for the corresponding average intensity

$$\frac{1}{\pi} \int_0^\pi \frac{(1-s^4)d\epsilon}{[2s \cos \epsilon - (1+s^2)]^2} = \frac{(1-s)(1+s^2)}{(1+s)^3}. \quad (7)$$

Along intermediate lines for which $\sin \zeta = 1$ the intensity never rises so high or falls so low. The average intensity is in this case determined by

$$\frac{1}{\pi} \int_0^\pi \frac{(1-s^4)d\epsilon}{(1-s^2)^2 + 4s^2 \cos \epsilon} = \frac{(1-s)^3}{(1+s)(1+s^2)}. \quad (8)$$

Before drawing any conclusions from these equations, we shall express equation (1) in the form of a series which will occasionally be found convenient when approximate results are sufficient and more especially when s is small.

For $s_1 = s_2$ we may write (1) in the form

$$I = J_1 J_2 = \frac{(1-s)^2 (J_2 - J_1)}{2s(\cos \delta_2 - \cos \delta_1)}$$

and apply the equation

$$\frac{1-s^2}{1-2s \cos \delta + s^2} = 1 + 2(s \cos \delta + s^2 \cos 2\delta + s^3 \cos 3\delta \dots), \quad (9)$$

which can be verified by adding the series on the right-hand side. Writing S_1 or S_2 for the series according as it contains δ_1 or δ_2 , we have

$$J_1 = \frac{(1-s)^2}{1-s^2} S_1; \quad J_2 = \frac{(1-s)^2}{1-s^2} S_2$$

and

$$J_2 - J_1 = \frac{1-s}{1+s} (S_2 - S_1),$$

from which we obtain

$$I = \frac{(1-s)^3}{1+s} \frac{S_2 - S_1}{2s(\cos \delta_2 - \cos \delta_1)}.$$

With the previous definition of ζ and ϵ , and writing

$$P_m = \frac{\sin m\zeta}{\sin \zeta}, \quad Q_m = \frac{\sin m\epsilon}{\sin \epsilon},$$

we find

$$I = \frac{(1-s)^3}{1+s} [1 + sP_2Q_2 + s^2P_3Q_3 + \dots].$$

Applying the equation

$$\sin(m+1)\theta - \sin(m-1)\theta = 2 \sin \theta \cos m\theta,$$

we easily find for odd values of m

$$Q_m = 1 + 2[\cos 2\epsilon + \cos 4\epsilon + \dots + \cos(m-1)\epsilon],$$

and for even values of m

$$Q_m = 2[\cos \epsilon + \cos 3\epsilon + \dots + \cos(m-1)\epsilon] \dots$$

The series for P_m is obtained by substituting ζ for ϵ . We shall use these equations for the calculation of the average intensity along a line of constant ζ . Noting in the first place that the average of Q_m is zero whenever m is even and equal to unity when m is odd, we may write down the average intensity at once as being

$$I = \frac{(1-s)^3}{s(1+s)} [s + s^3 \cos 3\zeta + s^5 \cos 5\zeta + \dots].$$

The series can be added up, and we finally have, writing $[I(\zeta)]$ for the average intensity, along the lines for which $\delta_1 - \delta_2$ is constant

$$[I(\zeta)] = \frac{(1-s)^3}{1+s} \cdot \frac{1+s^2}{1+s^4-2s^2 \cos 2\zeta} \dots \quad (9)$$

The maximum average is obtained when ζ is a multiple of π , and the minimum when ζ is an odd multiple of $\frac{\pi}{2}$.

In these two special cases we have already obtained the result by direct integration (see equations (7) and (8)). The ratio of the minimum to the maximum average intensities is

$$[(1-s^2)/(1+s^2)]^2.$$

Equation (3) shows that ϵ and ζ are interchangeable, so that we have along the lines for which $\delta_1 + \delta_2$ is constant

$$[I(\epsilon)] = \frac{(1-s)^3}{1+s} \frac{(1+s^2)}{1+s^4-2s^2 \cos 2\epsilon}.$$

The intensities along the circles at which δ_2 is constant are given by (1), and we find the average intensity either by integration or by making use of the series in (9):

$$[I(\delta_2)] = \frac{(1-s)^3}{(1+s)(1+s^2-2s \cos \delta_1)},$$

which has a maximum value of $(1-s)/(1+s)$ and a minimum

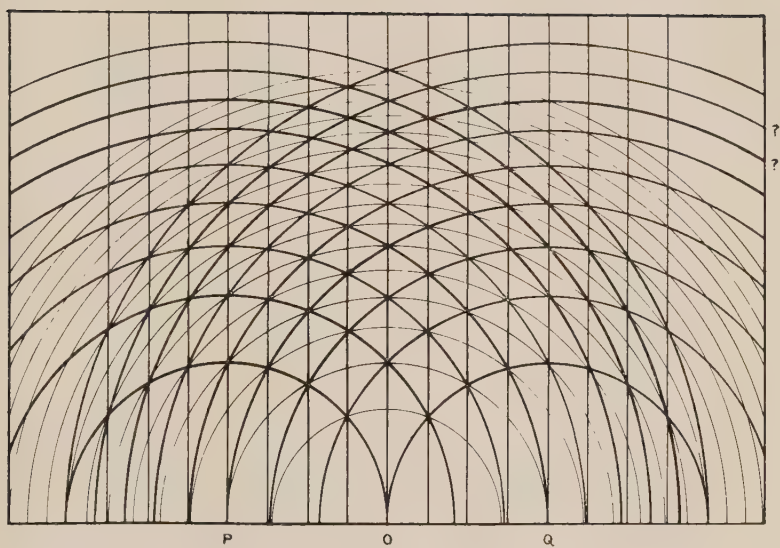
value of $(1-s)^3/(1+s)^3$, the ratio of the minimum to the maximum being $(1-s)^2/(1+s)^2$.

I have entered at some length into the question of these average intensities in order to form some judgment as to the interpretation which ocular vision would give to these overlapping circles and lines. A photograph was kindly taken for me by Mr. Twyman with two Fabry and Perot plates of equal thickness and slightly inclined to each other. Most prominent in the picture are the sets of overlapping circles which coincide with the circles due to each plate separately. The circles having O (see Pl. XII.) as centre, along which $\delta_1 + \delta_2$ is constant, are not visible at all, and the straight lines for which $\delta_1 - \delta_2$ has constant value are well shown in some of the outlying parts of the field. The photographs are not, however, as clear as could be wished, and show signs that the illumination was not uniform.

Mascart, in his 'Optics,' vol. i. p. 455, gives a picture of two sets of circles crossed by strongly-marked straight lines, without any sign of the set of circles for which $\delta_1 + \delta_2$ is constant. The optical arrangement which gave this pattern is not very clearly described, but so far as I can understand its essential part approximates to that obtained from two plates, one of which acts by reflexion and the other by transmission. Some allowance should be made in a drawing for the probable omission of the less striking parts of the picture. We may conclude, however, that the circles of constant ϵ do not strike the eye as those of constant ζ or δ . Some explanation is necessary to account for this. It will be remembered, of course, that each line of maximum average intensity is subject to fluctuations, the amount of which may be judged by an inspection of the accompanying table. This gives for four values of the reflecting power of s and different values of $(\delta_1 + \delta_2)$ the calculated intensities, when $\delta_1 - \delta_2$ is equal to zero or a right angle. These are the two values of ζ for which the intensity is respectively greatest and least. The average intensities are given at the bottom of the table, and the numbers in square brackets indicate the ratio of these averages. As ζ and ϵ are interchangeable, there is no reason here why the circles ($\zeta = \text{constant}$) should be less prominent than the straight lines at which ϵ is constant. In the lowest row I have entered the average intensities and their ratio for the circles at which $\cos \delta$ is either plus or minus unity. It is seen that there is along these lines a greater contrast between the circles of maximum and minimum light which may account for their greater

TABLE.

ϵ .	$s=2$.		$s=4$.		$s=6$.		$s=8$.	
	$\zeta=0$.	$\zeta=90^\circ$.	$\zeta=0$.	$\zeta=90^\circ$.	$\zeta=0$.	$\zeta=90^\circ$.	$\zeta=0$.	$\zeta=90^\circ$.
0°	1.000	.379	1.000	.096	1.000	.014	1.000	.001
15959	.382	.864	.100	.634	.015	.180	.001
30852	.393	.594	.109	.249	.017	.025	.001
45714	.409	.367	.126	.098	.023	.006	.001
60580	.417	.224	.150	.044	.033	.002	.002
75467	.410	.143	.173	.023	.050	.001	.005
90379	.444	.096	.184	.014	.062	.001	.012
105314	.440	.069	.173	.009	.050	.000	.005
120266	.417	.053	.150	.007	.033	.000	.002
135234	.409	.044	.126	.005	.023	.000	.001
150213	.393	.038	.109	.004	.017	.000	.001
165202	.382	.035	.100	.004	.015	.000	.001
180198	.379	.034	.096	.004	.014	.000	.001
Averages ζ481 [.853]	.410	.254 [.523]	.133	.133 [.221]	.029	.060 [.048]	.003
Averages δ667 [.444]	.296	.429 [.184]	.079	.250 [.062]	.016	.111 [.012]	.001



visible prominence. We have, further, to remember that the distances from maximum to minimum, as measured by the angular differences of the variables, do not correspond to equal linear distances in the pattern. It will be noted, *e. g.*, that the first circles with P and Q as centres will, when completed below the central line PQ, have 14 maxima, while the second circle having O as centre, which has the same diameter, has only 8 such maxima. This is probably the reason that in the grouping of the visible maxima of light the eye prefers to follow the lines along which the maxima are closer together. Further experiments with more perfect adjustment seem to be desirable.

In this communication only one of the several variations of the problem has been discussed in considerable detail, but there will be no difficulty in extending the investigation to light reflected from the plates instead of being transmitted. I may have another opportunity of treating the case where the two plates have not the same thickness, or when a small difference of thickness is partly compensated by a third plate.

August 11th, 1924.

Note.—I cannot help remembering that this is the fiftieth anniversary of the publication of the first of my papers that have from time to time appeared in the *Philosophical Magazine*.
A. S.

LXII. *Second Memoir on the Determination of the Curvature Invariant of Space-Time.* By L. SILBERSTEIN, *Ph.D.**

IN my first paper on this subject (*Phil. Mag.* for May, pp. 907–918) the case of radial inertial motion in de Sitter's space-time was considered. The rigorous spectrum-shift formula there deduced was

$$D \equiv \frac{\delta\lambda}{\lambda} = \gamma [1 \pm \sqrt{1 - \cos^2 \sigma / \gamma^2}] - 1, \dots (1)$$

with γ written for the integration constant

$$\gamma = \cos^2 \sigma \cdot c \, dt/ds \, \dagger. \dots (2)$$

Having unnecessarily limited myself to stars passing, in the

* Communicated by the Author.

† In the first paper, p. 910, line 11, $\cos \sigma$ is a misprint for $\cos^2 \sigma$.

future or the past, through the Sun as observing station with a velocity $v_0 = c\beta$, I wrote for this constant $(1 - \beta^2)^{-\frac{1}{2}}$ and considered it, therefore, as essentially greater than unity. Thus the working formula, for small σ and β , became

$$D^2 = \sigma^2 + \beta^2, \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

with $\beta^2 > 0$, giving rise to incidental remarks to the effect that $|D| \geq r/R$ or that, if the world-radius R be determined from a distant celestial object, neglecting its β , the value of R is underestimated. Thus also, if a single remote object were to show a rather small or a vanishing Doppler effect, it would rule out the R -value based on no matter how numerous other objects.

Now, Mr. P. Du Val in a recent private letter has drawn my attention to the possibility of $\gamma < 1$, corresponding, that is, to radial orbits *not* passing through the Sun, and I feel the more grateful, as his remark has enabled me to remove once for all the aforesaid difficulty or prospective danger.

In fact, by (2), and since $ds^2 = \cos^2 \sigma \cdot c^2 dt^2 - dr^2$,

$$\gamma = \frac{\cos^2 \sigma}{\sqrt{\cos^2 \sigma - v^2/c^2}}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $v = |dr/dt|$. Thus, if the star's orbit does pass through the Sun, $\gamma = (1 - \beta^2)^{-\frac{1}{2}}$, as before. But if it does not, and if at its "perihelion"

$$r = r_m = R\sigma_m,$$

we have, owing to $v_m = 0$,

$$\gamma = \cos \sigma_m.$$

If this be introduced into (1), the approximate formula for small σ_m becomes

$$D^2 = \sigma^2 - \sigma_m^2 = \frac{r^2 - r_m^2}{R^2}, \quad . \quad . \quad . \quad . \quad . \quad (1b)$$

as an alternative to (1a). Thus for any object $|D|$ may be either greater or smaller than r/R , without contradicting the R -value based on other material. Nay, we can have $D=0$ even for a very distant star or cluster, if it just happens to pass through its perihelion or, practically, if $r - r_m$ does not exceed a hundred light-years or so. As long as we confine our attention to radial motions, both cases, with the corresponding formulæ (1a) or (1b), appear equally likely. Consequently, in a correlation table, with $|D|$ as ordinates plotted against r as abscissæ, the

representative points, while showing a tendency to crowd near a straight line $|D| = r/R$ drawn through the origin, may be scattered both above and below this line, without invalidating the adopted R -value.

Such a correlation table, based upon all the existing data for objects not nearer than several thousand parsecs, will be given and discussed in the sequel.

Our next task, however, is to give up even the limitation to radial motions. In fact, such motions of stars, although very convenient to the mathematician, as they require him to deal only with two dimensions (r, t) , are extremely unlikely to cover any actual case of a celestial object. Not one in many thousand of such objects can be reasonably expected to move just away or just towards the Sun, or even only the region of the solar system. And, although the transversal component of motion will give only a non-observable second-order effect, yet the radial velocity component v_r (which is practically responsible for the whole effect) may, for oblique motion, be a more complicated function of distance than for purely radial motion.

Let us, therefore, consider the general case of any, oblique, inertial motion of a star S relatively to the Sun, with any perihelion distance $r_m = R\sigma_m$.

As is well known, any such orbit is plane, though not a straight line of the elliptic space. It will be convenient to place the origin of coordinates, r, θ , at S , as the sending station of light signals. Then the proper time s' of the star will be identical with the system-time, while that of the observer, reduced to the Sun, will be given by

$$ds^2 = \cos^2 \sigma \cdot c^2 dt^2 - dr^2 - R^2 \sin^2 \sigma \cdot d\theta^2, \quad \dots \quad (4)$$

and the Doppler effect will be determined by

$$D = \frac{ds}{ds'} - 1, \quad \dots \quad (5)$$

as explained in the first paper. The equations of the observer's world-geodesic, or of free motion, are

$$\frac{R}{c} \frac{d\sigma}{dt} = \pm \cos \sigma \sqrt{1 - \frac{\cos^2 \sigma}{\gamma^2} - \frac{p^2 \cot^2 \sigma}{R^2 \gamma^2}} = \pm \frac{v_r}{c}, \quad (6a)$$

$$\frac{d\theta}{dt} = \frac{cp}{\gamma R^2} \cot^2 \sigma, \quad \dots \quad (6b)$$

where γ, p are integration constants,

$$\gamma = \cos^2 \sigma \cdot c \, dt/ds, \quad p = R^2 \sin^2 \sigma \cdot d\theta/ds. \quad \dots \quad (6c)$$

We may notice that the corresponding orbit may be written

$$\sin^2 \sigma \left[1 + \frac{2-A}{A} \frac{\cos 2\theta}{\cos 2\theta_p} \right] = \frac{2}{A},$$

where $A = 1 + (\gamma^2 - 1)R^2/p^2$, the angle θ being counted from the axis of symmetry or the perihelion, and $\pm \theta$ being its value where the orbit, resembling an hyperbola, meets the star's polar. But this integrated form of the orbit will not be needed for the purpose in hand, which is the evaluation of ds corresponding to ds' .

The light rays issuing from the star as origin are simply the straight radii vectores $\theta = \text{const.}$ The wave fronts are spheres, $r = \text{const.}$, centred at S . Thus, let such a wave start from S at $t = \alpha$, and another at $t = \alpha + d\alpha$.

The first of these waves will reach the observer at $P_1(r, \theta)$ at an instant t_1 , and the second at $P_2(r + dr, \theta + d\theta)$ at $t_2 = t_1 + dt$. The star's proper time elapsing between the two signals being $ds' = c d\alpha$, we require ds , the observer's proper time elapsing between the receiving of the first and the second signal. Now, by the first of (6c), the element (4) can be written

$$ds^2 = \frac{R^2(d\sigma^2 + \sin^2 \sigma d\theta^2) \cos^2 \sigma}{\gamma^2 - \cos^2 \sigma}. \quad (7)$$

It remains to express $d\sigma, d\theta$ in terms of $d\alpha = ds'/c$.

The propagation of light from S being ruled by $\cos \sigma \cdot c dt = R d\sigma$, we have

$$c(t_1 - \alpha) = \int_0^\sigma R \sec \sigma d\sigma, \quad c(t_2 - \alpha - d\alpha) = \int_0^{\sigma + d\sigma} \text{idem},$$

whence $c(dt - d\alpha) = R \sec \sigma d\sigma$, i. e.,

$$c dt = ds' + R \sec \sigma d\sigma.$$

Eliminate dt by using (6a), thus finding $d\sigma$ in terms of ds' . Next find $d\theta/d\sigma$ by dividing (6a) by (6b), and substitute $d\sigma, d\theta$ thus determined into (7). Then, after some very simple reductions, the result will be

$$\frac{ds}{ds'} = \frac{\cos^2 \sigma}{\gamma} : \left[1 \mp \sqrt{1 - \frac{\cos^2 \sigma}{\gamma^2} \left(1 + \frac{p^2}{R^2 \sin^2 \sigma} \right)} \right],$$

which is the required ratio of the proper times. The signs $-$ and $+$ correspond to receding and to approaching motion respectively, and $r = R\sigma$ is the distance of the

observer from the star at the instant of taking its spectrogram*.

Ultimately, therefore, by formula (5), the rigorous value of the Doppler effect, for a star and an observer endowed with *any inertial motion*, will be

$$D = \frac{\cos^2 \sigma / \gamma}{1 \mp \sqrt{1 - \frac{\cos^2 \sigma}{\gamma^2} \left(1 + \frac{p^2}{R^2 \sin^2 \sigma}\right)}} - 1. \quad (8)$$

For $p=0$ our previous formula (1), relating to the sub-case of radial motion, reappears. The integration constants γ and p , whose values may vary from star to star, are originally defined by (6c). They may be conveniently expressed in terms of the shortest distance $r_m = R \sigma_m$ and of

$$v_m = \left(R \sin \sigma \frac{d\theta}{dt} \right)_m,$$

the velocity of the star at the perihelion. If β_m is written for v_m/c , we have

$$p = \frac{R \beta_m \sin \sigma_m}{\sqrt{\cos^2 \sigma_m - \beta_m^2}}, \quad \gamma = \frac{\cos^2 \sigma_m}{\sqrt{\cos^2 \sigma_m - \beta_m^2}}, \quad (9)$$

and, for the semi-amplitude θ_p of the orbit,

$$\tan \theta_p = \frac{\beta_m}{\sin \sigma_m}. \quad (9a)$$

The upper and the lower signs in (8) correspond to a motion which, at the moment of observation, is receding or approaching respectively. Introducing v_r , the radial velocity component at the moment of observation, we may write equivalently, by (6a),

$$D = \frac{\cos^2 \sigma}{\gamma \left[1 \mp \frac{v_r}{c} \sec \sigma \right]} - 1. \quad (8')$$

Finally, notice that at the perihelion, where $v_r=0$, the last equation gives, by the second of (9), $D_m = \sqrt{\cos^2 \sigma_m - \beta_m^2} - 1$, which is, in both σ_m and β_m , a second-order effect, as might have been expected. That this effect is negative or a blue-shift, need not surprise us. For, the source being at

* Which "instant" in all actually interesting cases (clusters, etc.) unfortunately extends over a hundred and more hours, this being the most serious difficulty of procuring the requisite data.

its perihelion at the moment of observation, it manifestly was approaching us at the instant of emission.

Thus far the rigorous spectrum-shift formula. Turning to practical applications, we can at any rate confound γ , as external factor in (8) or (8'), with unity. For in all cases of actual interest β_m^2 and σ_m^2 are negligible in presence of 1. The same remark applies to σ as entering through $\cos^2 \sigma$ in the numerator and through $\sec \sigma$ as factor of v_r in (8'). We are thus left with

$$D = \left(1 \mp \frac{v_r}{c}\right)^{-1} - 1,$$

and since v_r^2/c^2 is again a negligible fraction of unity, our formula ultimately becomes

$$D = \pm \frac{v_r}{c}, \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

which has the appearance of the classical Doppler formula. If we retain this as our working formula, the only innovation consists in v_r being a function of distance, namely, by (6a), to the required degree of approximation,

$$\left(\frac{v_r}{c}\right)^2 = 1 - \frac{1 - \sigma^2}{\gamma^2} \left(1 + \frac{p^2}{r^2}\right),$$

where, by (9),

$$\frac{1}{\gamma^2} \doteq 1 + \sigma_m^2 - \beta_m^2,$$

and similarly for p^2/γ^2 .

Thus, ultimately, our working formula will be

$$D^2 = \left(1 - \frac{r_m^2}{r^2}\right)(\sigma^2 + \beta_m^2), \quad . \quad . \quad . \quad (10)$$

with the previous coordination of the signs, or

$$v_r^2 = \left(1 - \frac{r_m^2}{r^2}\right)(H^2 + v_m^2).$$

Notice that, to this degree of approximation, the name "radial velocity" given to the measured spectroscopic effect cD continues to be a perfectly correct one.

For $r = r_m$ formula (10) gives at once $D_m = 0$, the transversal effect as one of the second order being already neglected. Finally, the special case of radial motion follows from (10). In fact, for a star passing through the observer's station we have $r_m = 0$ and $v_m = v_0$, so that

$c^2 D^2 = c^2 \sigma^2 + v_0^2$, and for one not passing, $v_m = 0$, $\sigma_m \neq 0$, and $D^2 = \sigma^2 - \sigma_m^2$, as before.

This settles all questions concerning our approximate formula (10), which for the time being differs but imperceptibly from the rigorous equation (8).

Turning now once more to the actual determination of the curvature radius, let us first put together the previous ten pairs of data, noticing, however, that the distance estimate of the Magellanic Clouds has been considerably increased in Shapley's last bulletin*, and adding three more items concerning globular clusters. The latter were originally discarded as showing the suspiciously small radial velocities, 10, 0, and -10 , with a P.E. of 25 to 50 km./sec. Now, however, in view of the possibilities afforded by the amplified formula, there is no reason for excluding them. This makes in all thirteen pairs of data r , D , which, to the best of my knowledge, exhausts all the existing material†. The radial velocities cD are given in km./sec., and the distances r , all due to Shapley, in kiloparsecs. The globular clusters are labelled by their N.G.C. numbers (New General Catalogue, *Mem. R.A.S.*, vol. xlix.). The Lesser and the Greater Magellanic Clouds are distinguished by *L.* and *Gr.*

Radial Velocities and Distances of Eleven Clusters and Two Clouds

Object	cD	r	$r : D $
6205	-300	11.1	11,000
6341	-160	12.3	23,100
6218	$+160$	12.4	23,250
*5904	$+10$	12.5	*
5272	-125	13.9	33,400
7078	-95	14.7	46,400
*7089	-10	15.6	*
*6626	0	18.5	*
5024	-170	18.9	32,200
6333	$+225$	25.0	33,300
L. Mag. Cl.	$+150$	25.0	50,000
6934	-350	33.3	28,500
Gr. Mag. Cl. ...	$+276$	35.0	38,000

* Bulletin 796, Harvard College Observatory.

† The data for a few more clusters may soon be available.

The three clusters showing exceptionally small effects are marked with asterisks. From the nil-effect of the last of these we can conclude only that this cluster is just passing through its perihelion. Similarly, for the remaining two, that they are comparatively near their perihelia, *i.e.* that their r/r_m differ but little from unity. If so, then the second term in (10) can be neglected and we can write $D^2 = 2r(r - r_m)/R^2$. Thus, if the transversal motions of these clusters were observed, r_m could be estimated and R could be determined from either cluster. But the proper motions of these distant objects not being accessible to observation, no R -estimate whatever can be based on these clusters taken by themselves.

With the exception of these three objects the values of the quotients $r : |D|$, again in kiloparsecs, are tabulated in the fourth column. If, as in the first paper, β_m^2 and r_m^2 were disregarded, these quotients would represent rough approximations to the R -value, with an arithmetical mean of the ten values $R = 31,900$ kiloparsecs or

$$R = 6.6 \cdot 10^{12} \text{astr. units.} \quad . \quad . \quad . \quad (11)$$

But since there are no good reasons for neglecting either β_m^2 in presence of σ^2 , or of r_m in presence of r , any such "mean" R -value can claim no more than a provisional validity.

A more satisfactory method of estimating the curvature radius, by means of all the data gathered in our table, seems to be the following one.

Since both β_m and r_m , integration constants, are independent of the actual distance r of a celestial object, their values and therefore also those of r_m/r and β_m^2 may be reasonably expected to have a random distribution over a group of objects picked out haphazardly, though all equidistant or nearly so. The means $\overline{\beta_m^2}$ would then be the same for two such groups, with different values of $\overline{r^2}$, provided each group contains a large number of objects. If so, and if all values of r_m/r from 0 to 1 are considered equally likely, then formula (10)—applied to the two groups, 1 and 2, say—will give at once

$$\overline{D_2^2} - \overline{D_1^2} = \frac{2}{3R^2} (\overline{r_2^2} - \overline{r_1^2}), \quad . \quad . \quad . \quad (12)$$

an equation for R in terms of actual distances and spectroscopic effects alone. Our thirteen objects are certainly too few to form only one such group. With the generous aid of friendly astrophysicists, I hope to gather in the near future

sufficient data for a somewhat reliable application of this statistical method. In the meantime, we cannot do better than split our scanty material into two groups, of *seven* and of *six* celestial objects, as shown by the horizontal line drawn across our table. This gives, in squared km./sec. and squared kiloparsecs,

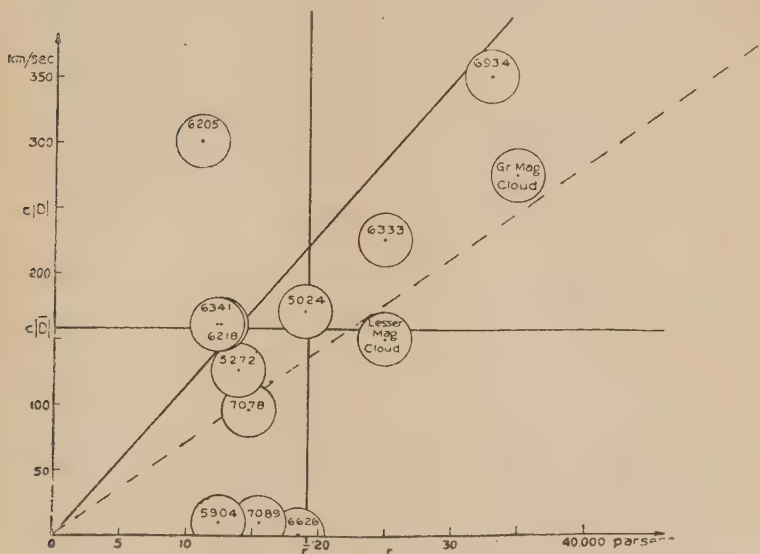
$$\overline{r_1^2} = 176.8, \quad \overline{r_2^2} = 713.9; \quad c^2 \overline{D_1^2} = 23,720, \quad c^2 \overline{D_2^2} = 50,120,$$

where, of course, no more than two or three figures are at all reliable, and, by (12), $R = 34,900$ kiloparsecs or

$$R = 7.2 \cdot 10^{12} \text{ astr. units, } \dots (12a)$$

which is somewhat greater than the value (11), but seems at any rate to deserve a higher degree of confidence.

RADIAL VELOCITIES & DISTANCES OF ELEVEN GLOBULAR CLUSTERS & THE MAGELLANIC CLOUDS



In addition to this, a graphical representation of the whole available material has seemed desirable. This is given in the accompanying diagram, in which the thirteen points (centres of labelled circles) have for their coordinates $r, c | D |$ the pairs of data of the preceding numerical table. The supplementary axes are drawn through the point, near "N.G.C. 5024," whose coordinates are the means of those of the thirteen representative points. That there is at all a correlation of the type: radial velocity increasing on the whole with distance, is shown well enough by the scarcity

or almost complete absence of points in the second and the fourth quadrants, in accordance with a well-known correlation criterion. The dotted line drawn through the origin has the equation $|D| = r/R$ with $R = 7.2 \cdot 10^{12}$ astr. units, as in (12 a), and this value of the curvature radius is, thus far, supported markedly enough by the tendency of crowding along this line, shown by six or perhaps eight celestial objects. The full line is superfluous in the present connexion.

Rochester, N.Y..

June 1, 1924.

Note added in proof-reading, August 19.

Since the above was printed, my attention was drawn to a fairly reliable distance estimate of the spiral nebula Messier 33, of known radial velocity, and Prof. V. M. Slipher was kind enough to give me his unpublished radial velocities of seven more globular clusters, the distances of which were already measured by Shapley. This has enabled me to add to the above correlation table eight more items. The complete table of 21 objects, containing a considerably strengthened evidence for a curvature radius of 7 to $8 \cdot 10^{12}$ astr. units, was shown in connexion with a paper read at the recent Toronto meeting of the British Association, and will be given, together with a full numerical discussion, in a later issue of this Journal.

LXIII. *A New Variety of Spectra.* By WILLIAM HAMILTON McVICKER, JOSEPH KENNETH MARSH, and ALFRED STEWART*.

WHEN an induction-coil discharge is passed through the vapours of carbon compounds, decomposition ensues; and the spectra emitted are merely those of carbon or its oxides. By selecting specially stable hydrocarbons and derivatives, Wiedemann and Schmidt† succeeded in obtaining spectra of continuous emission in the case of ten carbon compounds; but as they were unable to extend their work to other organic substances, and as, further, their examination was confined to the visible region, the results

* Communicated by Professor Stewart.

† Wiedemann & Schmidt, *Ann. d. Physik*, lvi. p. 29 (1895).

obtained by them brought nothing of much importance to light in this branch of spectroscopy.

By employing a large Tesla transformer instead of an induction coil, and by utilizing a quartz spectrograph, we* have overcome the difficulties encountered by previous workers and have now obtained a series of spectra, each of which is characteristic of the carbon compound by which it is emitted: and thus a new constitutional property has been added to the list which contains refractive index, magnetic rotation, absorption spectra, etc.

In order to illustrate the results which we have obtained, a description of the Tesla-luminescence spectrum of benzene is given below. An examination of this spectrum was originally made with the help of a Hilger quartz spectrograph, size C; but since these initial results were published† we have re-examined the spectrum with an instrument of greater dispersion; and we have also succeeded, by a modification of the experimental conditions, in identifying certain bands in the extreme ultra-violet which were not detectable by the original method. The figures given in the present paper are thus much more complete than those in the earlier communication.

1. Apparatus.

The quartz spectrograph employed was the large size constructed by Bellingham and Stanley, which gives a complete spectrum about half a metre long, taken in three sections. Extra rapid plates of various makes have been used. When the spectrum extends into the visible, Panchromatic plates developed with the help of Desensitol have been utilized for this region of the spectrum. The exposure varies very considerably owing to the different intensities of the spectra of various substances. Thus while benzene requires about fifteen minutes' exposure with an extra rapid plate, the spectrum of anthracene can be obtained in twenty seconds with an ordinary plate, and its intensity appears to be almost the same as that of the background of an iron arc under the same conditions.

The cell in which the vapour is photographed is constructed entirely of quartz, with a plane quartz window at the end of a straight tube which is laid in line with the spectrograph axis. This tube contains an internal electrode formed of a

* Trans. Chem. Soc. cxxiii. pp. 642, 817, 2147 (1923).

† *Ibid.*

glass tube filled with mercury ; and the second electrode is a piece of metal foil wrapped round the outside of the quartz tube. A bulb is blown on to the quartz tube near the window ; and an exit for the vapour is provided at the other end of the straight tube, so that the vapour of the substance under examination (which is volatilized in the bulb) can be rapidly passed through the cell in a continuous current. Electrical heating is applied to the straight tube when high-boiling substances are under examination.

The exit-tube of the cell is connected, through a trap, with a mercury vapour-pump, and this in turn is connected with a motor-driven oil-pump.

The current is supplied by a high-frequency apparatus furnished by the Medical Supply Association, Ltd. It is air-insulated, and its secondary and primary are directly coupled together. It contains seventy coils ; and the primary circuit is variable up to twenty-four coils. There are two leyden-jars of about one litre capacity each. The spark-gap has zinc knobs. With this apparatus, driven by means of a 12-inch induction coil, a steady discharge passes, as in an ozonizer, across the vapour contained in the cell.

Variations of pressure and temperature have been found to exert very minor effects in the case of the benzene spectrum. The discharge passes freely and without decomposing the compound to any extent at pressures of 65 mm. and below. At ordinary pressure the discharge is accompanied by sparks and the benzene decomposes, yielding fragments of the carbon spectrum.

2. *The Tesla-luminescence Spectrum of Benzene* *.

The Tesla-luminescence spectrum of benzene consists of over seventy fine bands, which appear to fall into eight groups. The first two of these—termed Group H and Group G in the annexed table—are apparently incomplete ; and it seems probable that the remaining bands of these groups are of feeble intensity, and are thus blotted out by the absorption of ultra-violet light by the benzene vapour itself.

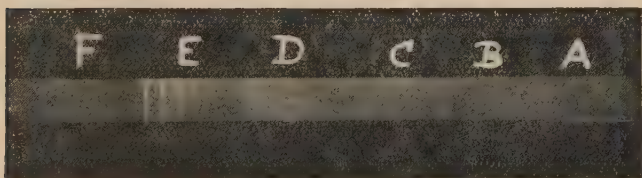
The next group, Group F, contains 12 bands ; then in turn follow Group E—the most complete of all—with 18 bands, Group D with 15 bands, Group C with 12 bands, Group B with 9 bands, and Group A with 5 bands. The brightest series of bands is to be found in Group E ; whi'st

* See accompanying figure.

the bands with the lowest wave-numbers in Groups D, C, B, and A become progressively more diffuse and difficult to read. On this account the positions of certain bands in Groups A and B have been read off the plates taken with the Hilger instrument, which shows them most clearly. These figures are given in round brackets in the table.

Some of the bands in Groups G and H were detected in the following manner. Instead of volatilizing pure benzene in the cell, a mixture of benzene and alcohol was placed in the bulb. Alcohol yields no Tesla-luminescence spectrum of its own, but acts in this case merely as a diluent for the benzene vapour. In this way, since the benzene exerts only its partial pressure in the vapour, it was possible to examine its spectrum under higher conditions of rarefaction than could be attained with benzene alone in the cell; and since

Fig. 1.



alcohol vapour is extremely diactic, we were thus enabled to reduce the degree of light-absorption due to vapour in the cell and so to penetrate further into the ultra-violet region. Figures obtained by this method are shown within square brackets in the table.

In addition to these bands, we have also observed very faint traces of bands in the blue region. These appear to correspond to certain members of a four-group system of twenty-five bands which attain their fullest development in the spectrum of benzaldehyde; but we have not included them in the table since they are so faint that no accurate readings of them are possible. A full list of these bands in the benzaldehyde spectrum has already been given by us in a previous paper*.

Examination of the table will show that the benzene spectrum exhibits a very apparent regularity. Omitting Groups H and G, which are obviously incomplete, inspection will show that each of the remaining groups contains six

* Marsh, McVicker, & Stewart, *Trans. Chem. Soc.* cxxiii. p. 2150 (1923).

bright bands (marked with asterisks) ; and it is evident that any one of the strong bands in, say, Group D has a congener in Group C with a wave-number 100 units higher. The same regularity is traceable in the case of the weak bands ; though the completeness of the system is marred by the absence of certain bands from Groups B and C, these bands being possibly too faint to be observed. In Group A the diffuseness of the bands makes it impossible to determine with exactitude whether any faint bands exist or not ; and in this group the readings are at best only approximate ones for the same reason.

The Wave-numbers of the Bands in the Tesla-luminescence Spectrum of Benzene.

Group A.	Group B.	Group C.	Group D.	Group E.	Group F.	Group G.	Group H.
					3663*	3763*	[3861*]
—	(3279)*	3372*	3471·5*	3570·5*	—	—	
				3584·5			
(3194)*	(3294)*	3389*	3486·0*	3586·0*	3685·0	—	
—	—	—	3492·0	3588·5	3692·0	—	
				3597·3	3699·0		
—	—	3401·0	3500·0	3599·0	3700·5		
			3503·3				
(3211)*	(3308)*	—	3507·0*	3608·0*	3710·0*	—	
—	3319·0	3419·0	3517·0	3616·0			
(3229)*	3322·5*	3421·0*	3529·0*	3618·5*	3716·0	—	[3914]
—	—	3424·0	3523·5	3624·0	3724·0		
				3625·0			
—	3334·0	3434·0	3534·0	3632·0	3732·0	—	[3931]
(3242)*	3336·5*	3436·0	3536·0*	3635·0*	—		
—	—	3439·5	3539·0	3641·0	3740·0	[3839·0]	
				3643·0		[3843·0]	
—	3351·0	3450·5	3550·0	3649·5	3749·0		
				3651·0		[3852·0]	
(3257)*	3354·0*	3454·0*	3553·0*	3654·0*	3753·0*		
—	—	3456·0	3556·0	—	—		

Figures in square brackets represent bands visible only when benzene vapour is mixed with alcohol vapour. Figures in round brackets were read from plates taken with a Hilger (c) spectrograph ; these bands are very diffuse and hence their position can only be given approximately. The whole spectrum increases in brightness from top to bottom of the table.

The existing data, however, are quite sufficient to suggest that the Tesla-luminescence spectrum of benzene in its main outlines consists of a series of at least eight band-groups, each of which reproduces with great exactitude the same system of bands and differs in position from its neighbours by approximately 100 units in its wave-numbers.

3. *The Fraunhofer Effect.*

Hitherto, the Fraunhofer effect has been confined to the cases of the vapours of elements such as sodium; but the discovery of the Tesla-luminescence spectrum of benzene has led us to an extension of this field into the spectra of compounds of complicated structure.

Hartley* examined the absorption spectrum of benzene vapour at various temperatures and pressures, and embodied his results in a map on which he plotted the positions of the various absorption bands observed by him. It has already been pointed out that owing to the diffuseness of certain bands in the Tesla-luminescence spectrum of benzene, absolute exactitude in measurement cannot be attained; and the same may be said of the determinations of position of absorption bands in benzene vapour. Nevertheless, even when all due allowance is made for this, it must be admitted that the positions of the two sets of bands coincide so closely as to show that each absorption band has a counterpart in one of the emission bands of the Tesla-luminescence spectrum. The following table contains the wave-numbers

Tesla Emission Bands.	Hartley's Absorption Bands.	Tesla Emission Bands.	Hartley's Absorption Bands.	Tesla Emission Bands.	Hartley's Absorption Bands.
3763	3761	3700	3700	3643	****
3753	3754	3699	****	3641	****
3749	3749-52	3692	3691	3635	****
3740	3738	3685	3683	3632	****
3732	3734	3663	****	3625	3621
3724	3722	3654	3656	3618	3617-18
3716	3716	3651	3650	3616	****
3710	3708	3649	****	—	—

of all the emission bands marked by Hartley on his map; and alongside of them we have placed the wave-numbers of all the emission bands observed by us in the same region

* Hartley, Phil. Trans. ccviii. A. p. 384 (1908).

of the spectrum *. Inspection will show at once that the figures in the two columns are identical within experimental error in practically every case.

With regard to the missing bands in the absorption spectrum, the positions of which are indicated by the asterisks, it may be pointed out that, although Hartley gives no bands in these positions on his map, an examination of the fuller tables included in his paper shows that he observed regions of absorption even at these points: so that the coincidence between the two sets of figures is even closer than appears from the table above.

The interpretation of these results admits of no doubt. The Tesla-luminescence spectrum of benzene vapour evidently represents a reversal of the absorption spectrum; so that for the first time it has been possible to exhibit the Fraunhofer effect in the case of a complex organic compound of known constitution. In view of the regularity of the benzene Tesla-luminescence spectrum, this seems to mark the opening of a very promising chapter in spectroscopic work; and it suggests that in future a mathematical treatment of absorption spectra may be possible from an entirely fresh point of attack.

4. *Fluorescence and Tesla-luminescence.*

A very complete examination has been made † of the fluorescence spectrum of benzene vapour excited by a mercury vapour-lamp. It was found that there was a very marked resemblance between the fluorescence spectrum and the Tesla-luminescence spectrum. The former is, however, much longer than the latter, as it penetrates further into the ultra-violet; and, further, the development of the so-called "blue bands" in the visible is much greater than in the case of the Tesla-luminescence spectrum, where they are so faint as to be detectable only with difficulty. It was found that some bands were developed in the fluorescence spectrum under a pressure of 60 mm., whereas in the case of the Tesla-luminescence the pressure had to be reduced to less than 2 mm. before the same bands appeared.

* The absorption spectrum extends into the far ultra-violet, whilst the Tesla-spectrum runs further towards the visible than the absorption spectrum does. Comparison is, of course, possible only in the spectral region in which the two spectra overlap each other.

† McVicker & Marsh, Trans. Chem. Soc. cxxiii. p. 820 (1803); Marsh, *ibid.* p. 3318.

5. *The Influence of External Conditions.*

Marsh and McVicker* have investigated the effect of altering the temperature and pressure at which the benzene vapour is examined; but it was found by them that even when these factors were varied over wide ranges the essential characteristics of the benzene spectrum remained unchanged. Alterations in the tuning of the Tesla transformer were also found to have no particular results.

It has already been pointed out above that when benzene is mixed with another substance which yields no Tesla-luminescence spectrum of its own, the benzene spectrum remains unaltered.

McVicker has investigated the effect of a powerful magnetic field upon the Tesla-luminescence spectrum of benzene, but so far the results have been negative, no change having been observed.

6. *The Tesla-luminescence Spectra of other Compounds.*

Up to the present we have examined the Tesla-luminescence spectra of over sixty compounds of the most varied character, and it is possible to say that each compound has its own special characteristics, so far as this emission is concerned. We have succeeded in drawing up certain general rules which appear to be valid with regard to the effects produced by changes in the constitution of compounds.

Saturated hydrocarbons, such as cyclohexane, seem incapable of yielding luminescence spectra, and the saturated fatty alcohols appear to show no emission. Aliphatic ketones and aldehydes emit a continuous faint spectrum between the wave-lengths 3500 and 4800, each compound having a spectrum of its own. Substitution in the benzene nucleus may produce either of two effects. If the substituent be a halogen atom or a nitrogroup, the benzene spectrum is completely blotted out and the compound shows no emission whatever; but if the substituent be a hydrocarbon radicle like the methyl group, or an amino-radicle, or an unsaturated group like $-\text{CHO}$, then the benzene spectrum is subjected to profound modification, whilst at the same time a fresh zone of emission appears in or near the visible. In the case of hydrocarbons containing condensed ring-systems like naphthalene or anthracene, the emission may become very intense and appear quite far up in the visible. Some

* Marsh & McVicker, Trans. Chem. Soc. cxxiii. p. 817 (1923).

heterocyclic compounds like pyridine, pyrrol, and thiophen, yield no emission spectra so far as our experience goes; though quinoline, isoquinoline, and tetrahydro-quinoline all yield spectra of varying intensities. It may be pointed out that in each of the last three cases a benzene nucleus is present in the molecule; possibly it forms the luminescent centre.

A large part of the apparatus used in this research was purchased from the Heron Fund of this University, and we wish to express our thanks to Mr. F. A. Heron, D.L. We also desire to acknowledge the assistance received from the Research Committee of the Chemical Society in the form of a grant.

The Sir Donald Currie Laboratories,
The Queen's University of Belfast,
Northern Ireland.

LXIV. *Application of a Thermionic Valve to the Measurement of the Damping of Vibrations of a Steel Wire.*
By FLORENCE M. CHAMBERS, M.Sc., Senior Demonstrator
in Physics, Queen's University, Belfast*.

Introduction.

IN the following will be found the results of some experiments on the damping of forced vibrations of a steel piano-wire, a question about which there seems to be little, if any, quantitative information available.

The idea is to get numerical values for the coefficient of the damping term in the equation of motion, and to examine its variation with pitch and with the method of supporting the wire.

The method employed was to measure the amplitude of forced oscillations under an impressed alternating force furnished by the oscillating current in the circuit of a thermionic valve.

As will be shown, the string was made to vibrate in a simple harmonic manner, and the results obtained apply to the damping of simple harmonic oscillations.

* Communicated by Professor W. B. Morton.

Theory of the Method.

The equation to damped, forced simple harmonic vibrations is

$$\ddot{x} + k\dot{x} + n^2x = C \sin mt$$

assuming friction proportional to velocity, where

$m/2\pi$ = frequency of impressed force,

$n/2\pi$ = natural frequency of the system.

From this equation we find

$$A^2 = C^2 / \{ (n^2 - m^2)^2 + k^2 m^2 \},$$

where A is the amplitude of the forced vibration.

A is maximum when $(n^2 - m^2)^2 + k^2 m^2$ is minimum, *i.e.* when $m^2 = n^2 - \frac{1}{2}k^2$.

Therefore at maximum

$$A^2 = C^2 / \{ k^2 (n^2 - \frac{1}{4}k^2) \}.$$

The ratio

$$\begin{aligned} A^2 / A_{\max}^2 &= k^2 (n^2 - \frac{1}{4}k^2) / \{ (n^2 - m^2)^2 + k^2 m^2 \} \\ &= a^2, \text{ say;} \end{aligned}$$

$$\therefore a^2 = (1 - \frac{1}{4}k^2/n^2) / \{ m^2/n^2 + (1 - m^2/n^2)^2 / (k^2/n^2) \}. \quad (1)$$

As will be seen later, k/n is of the order from .001 to .0005 for a steel lathe-bed, and from about .003 to .001 for wooden sonometers, so the quantity $\frac{1}{4}k^2/n^2$ may be neglected compared with 1.

It is then found from above equation that

$$k/n = a(1 + m/n)(1 - m/n) / \sqrt{1 - a^2 \cdot m^2/n^2}.$$

But m/n is approximately in actual cases equal to 1. (It ranges from .996 to 1.004.)

Therefore $1 + m/n = 2$ and $a^2 m^2/n^2 = a^2$;

$\therefore k/n$ is very nearly

$$2a(1 - m/n) / \sqrt{1 - a^2}. \quad (2)$$

Plan.

Two ways were adopted for finding the k/n of the string in different circumstances:—

(1) Values of a were assumed and the corresponding values of m/n worked out for each of a series of assumed values of k/n . A set of m/n and a curves was plotted from

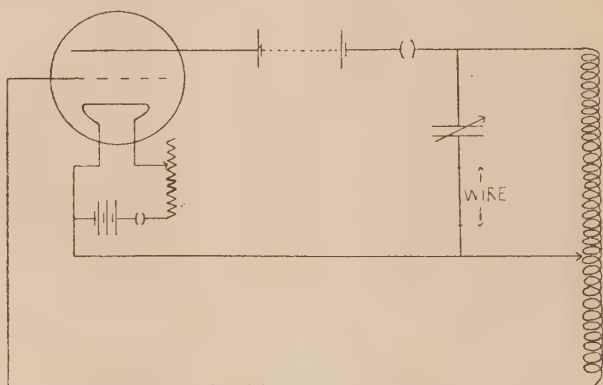
these for the different values of k/n , and the observed points were plotted on the same paper. Thus it was possible to find approximately the range of k/n for a given set of results. This method was used in the initial experiments, where, owing to necessary experimental difficulties, great accuracy of observation was not possible.

(2) From the observed corresponding values of a and m/n , k/n was worked out, using equation (2), and the mean k/n for each set of observations found. This method was applied to the more accurate observations taken on a steel lathe-bed.

Experimental arrangement.

The simple harmonic vibrations were maintained by using the oscillatory current in the circuit shown (fig. 1),

Fig. 1.



with the string in series with the condenser, so that the oscillating current passed through the string. The latter was placed between the flat poles of an electromagnet specially made for the purpose and run off the town mains (direct current). The variable coil was also specially made of large self-inductance, with a movable core of iron wires, so that low frequencies could be obtained. The pitch of the oscillating circuit was changed by varying the condenser and varying the number of turns in the secondary and primary coils. Fine adjustments in pitch could be made by moving the iron core.

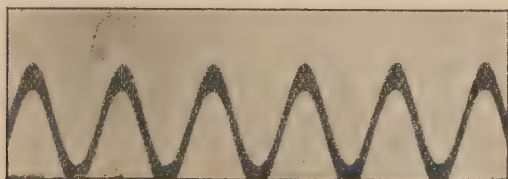
Throughout the experiments on wooden sonometers placed horizontally, there were always variations of amplitude taking place in the course of observations, and these made

accurate readings difficult. The worst variations were abolished by substituting a battery of small accumulators for the unreliable town-mains to supply the anode voltage. The small changes which remained depended on small changes in tension of the wire, due probably partly to friction in the pulley and small yielding of supports, partly to small temperature changes in the wire on account of the current passing through. Once the oscillating circuit has settled down, a galvanometer shows that the current keeps constant throughout an experiment; so the small changes in amplitude are not a result of a varying applied force.

Test of Simple Harmonic Character of Vibration.

The vibration form of the string was first investigated by mounting the string in a dark room and photographing on a moving plate the motion of the string's shadow across an illuminated slit, after the manner of Krigar Menzel and Raps. This gives the displacement-time curve of a point on

Fig. 2.



the string. The photograph (fig. 2) is an example of the curves obtained at different points of the string with different positions of the electromagnet. All the photos taken showed curves of the same form.

On measuring up an enlargement of one of these photos, plotting out the numbers obtained, and comparing the resulting curve with a sine-curve of the same size, the two were found to coincide almost exactly.

Several sine-curves were also obtained by plotting the amplitude (measured by the eyepiece-scale of a microscope) against the distance from one end.

The above shows that we are justified in assuming that the vibrations of the string are simple harmonic.

Method of taking observations.

As we have now at our disposal a method of forcing the string to vibrate in a simple harmonic manner, and as

the pitch of the oscillations in the circuit is adjustable to any value, k/n may be found as follows:—

The string and the oscillating circuit are tuned to a pitch about four vibrations per second above or below the pitch of a standard fork. A series of corresponding amplitudes and pitches are found; the amplitude is observed on the eyepiece-scale of a microscope. The pitch is found by observing the number of beats per second between the notes of the string and the fork. a is obtained by dividing amplitude by maximum amplitude; m/n by dividing frequency by frequency at maximum amplitude.

k/n is then found as explained from equation (2).

Details of Experiments.

The first experiments were made on two wooden sonometers, placed horizontally on the bench. The string used was 29 s.w.g. piano-wire, about 60 cm. long. The string vibrated in a vertical plane.

Sonometer A had a screw for adjusting tension of the wire. With Sonometer B the tension was adjusted by weights hung from the string, which passed over a pulley. On both sonometers the string passed over two bridges.

The points of the damping curve for A—about 70 in number, taken on different days—were found to lie between theoretical curves corresponding to $k/n = .0020$ and $k/n = .0015$, but nearer the $.0020$ curve, at a pitch of about 256 vibrations per second. The accuracy of the observations is not sufficiently great under experimental conditions to make it worth while working out k/n for each point and taking the mean k/n .

Sonometer A had a crack in the wood, so we might expect the damping to be greater than in the case of Sonometer B. This was found to be actually the case. The points for B at the same pitch lie close to the curve of $k/n = .0014$.

Further observations made on Sonometer B, with more precautions, especially in allowing for the string's thickness, gave the result at pitch 256 $k/n = .0015$, and at pitch 384 $k/n = .0030$.

A set of observations on the same sonometer at pitch 320 showed k/n about equal to $.002$. In all cases a large number of observations were taken.

Thus it is found with a wooden sonometer that as the pitch increases the ratio of damping factor to frequency also increases. The damping factor, k , increases very

rapidly with rising pitch. The amplitude of the vibration falls off rapidly with rising pitch, and a one-inch objective had to be used to observe the amplitude at pitch 384.

In order to obtain more accurate results for k/n than was possible on account of the small and continual changes in amplitude mentioned above, the sonometer was mounted vertically. The string was fastened as before by a peg, passed over a bridge, and at the lower end was a hook, from which weights were hung.

This was first tried on Sonometer B. It was found now that once the oscillating current had settled down to its steady value, the amplitude of the string would remain steadily at the same value for as long as it was left, the small variations in amplitude having disappeared. This confirms the former conclusion that these variations were due to changes in tension.

It was possible now to make accurate observations, and the value of k/n was worked out for each reading in turn in every case. Henceforward it is found that the mean deviation of k/n from the mean value of k/n obtained for any one set of observations varies from about 1 to 5 per cent.

In order to get as clear a mark as possible on the string for observing the amplitude, a scratch was made on the wire with emery paper or a penknife, and this, illuminated by a lamp, gave a sharp bright line seen through the microscope.

For Sonometer B it was found here that at pitch 256 $k/n = \cdot 00103$ —considerably less than the value for the same sonometer mounted horizontally. This is to be expected, as in the present case only one bridge is communicating energy from the string to the sound-box. On another day, k/n at the same pitch for this sonometer was found to be $\cdot 000813$, showing that when we have a freely-suspended weight other factors come into play besides the pitch in determining the damping. This is referred to later, in connexion with a lathe-bed.

The damping of a string mounted on a massive lathe-bed was next investigated. The lathe-bed was mounted vertically on a stand of concrete, whose foundations were in the ground. This gives a very massive support for the string, and one would expect very small damping, as there can be little motion of the ends.

The damping was actually found to be small, and the note heard was so extremely faint (although the string's amplitude was as great as ever) that often one could only hear it properly by placing the ear against the lathe-bed. Some of

the experiments at the lower pitches had to be carried out in the evenings between 8 and 10 P.M., as there was too much noise during the day to hear the beats at all.

Observations were first of all made on the string at pitch 256. The upper end of the string passed over a blunt steel edge, and was fastened to the back of the bed.

It was found that the readings of each set were consistent among themselves, as before (deviation from mean less than 5 per cent.). The damping factor, however, varied from one set to another at the same pitch. It was thought that this might be due to changing the weights; but with the same weight hung on, so as to give the total suspended mass different shapes, the damping factor varied. The table (Table I.) gives some results at pitch 256.

TABLE I.

$k/n \times 10^3$	1.046	.977	.887	.875	.826	.892
Load, in kg.	12.4	12.4	9	15.7	13.2	9

Apparently there is no relation between k/n and the weight, or if there is such a relation it is masked by the change in end-conditions brought about by altering the configuration of the weights with respect to the string.

An attempt made at this stage to find how the damping depended on the pitch was unsuccessful: there was little change in k/n with rising pitch; such changes as there were were inconsistent with each other; it was impossible to change the pitch without altering the end-conditions sufficiently to account for any change in damping without considering pitch at all.

Readings were as in Table II.

TABLE II.

Note.....	C	D	E	F	F	F	F
$k/n \times 10^3$826	.809	.818	1.045	1.059	1.016	.887

The last value for F was obtained after taking off the weights and putting them on differently.

A further attempt was made to keep end-conditions constant by gripping the string between steel chucks. The old trouble of varying amplitude due to small changes in

tension (probably this time entirely due to temperature-changes in wire) reappeared, so much exaggerated on account of the extremely small damping that it was impossible to take readings.

Finally, the only way of approaching the ideal of a string fixed at both ends seemed to be to hang a very heavy single weight on the end of the string, the weight being arranged each time so that its disposition with respect to the direction of vibration of the string should be the same throughout the experiments. The string (this time a thicker wire, 27 s.w.g.) was gripped at its upper end in two steel jaws—part of a fitting belonging to the lathe-bed. The wire was about 90 cm. long, and from the hook at the lower end hung a weight of 20 kg.

The damping was now smaller than ever (probably nearly all air-damping), and the difficulty of maintaining the maximum amplitude for any length of time very great. One may observe accurately the maximum amplitude, but there is great difficulty in observing accurately the exact *pitch* at maximum amplitude. This was found finally by taking the mean of the two pitches at the same amplitude on either side of the maximum. The average of three such values at different amplitudes (*i. e.* the mean of six readings) gives the mean pitch at maximum amplitude.

Readings of amplitude and pitch were taken as described above—six readings in each set,—and the mean value of k/n obtained. This was done for frequencies C (253), C (259), D (284), E (316), E (323.5), F (337), G (380), A (423), B (477).

The forks used for pitches other than C were not standard forks, and may not be correct to one vibration. This is not a matter of great importance, as in calculating k/n the *ratio* only of the frequencies of forced and free vibrations appears.

To get a sustained note from the small forks which were not fitted with resonators, in order to count beats easily, each fork was mounted in turn with its prongs at the mouth of an adjustable pipe closed at one end with water. The pipe, tuned to the fork, acted as a very efficient resonator, and after bowing the fork the note could be heard in the room for over a minute.

The results obtained are shown on the two curves. Fig. 3 shows k/n plotted against the frequency. It will be seen that k/n decreases at first rapidly, then more slowly with

increasing frequency. Fig. 4 shows k and frequency. The damping factor k increases with rising pitch. Fig. 5 shows a characteristic a and m/n curve. It was taken for the lathe-bed, at pitch 256, with a weight of 12.4 kg. hung on the string.

Fig. 3.

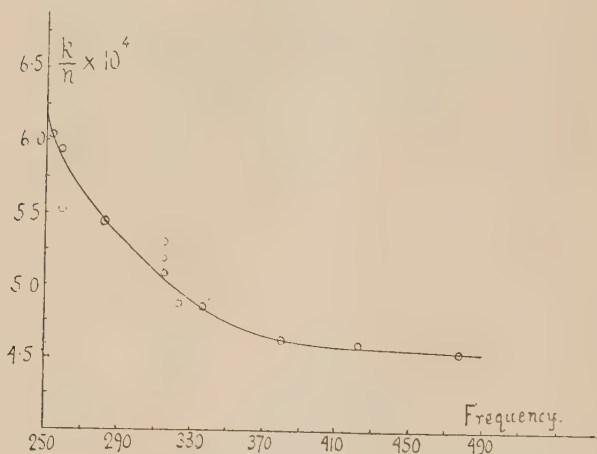
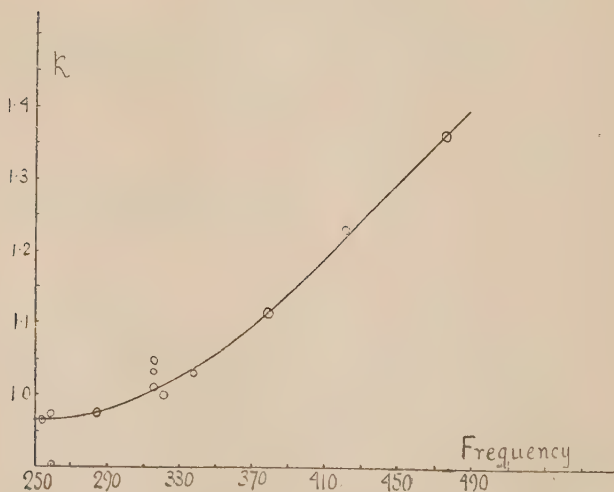


Fig. 4.



Summary of Results.

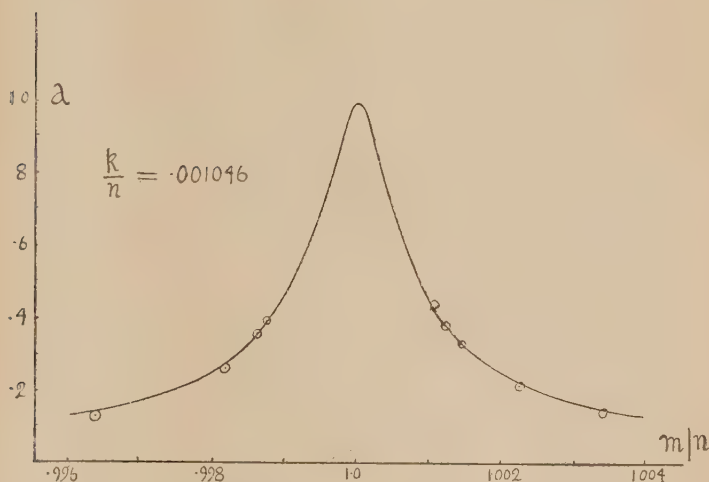
(1) Numerical results have been found for the "damping coefficient" for a steel wire mounted on different supports, and at different pitches.

(2) Damping of a cracked wooden sonometer is greater than for another sonometer without a crack.

(3) For a wooden sonometer, as pitch rises, the factor k/n increases. There is therefore a very rapid increase of the damping factor k with rise in pitch.

(4) When the wooden sonometer is mounted vertically, the string passing over one bridge instead of two, the damping is less than with the same sonometer mounted horizontally.

Fig. 5.



(5) For a massive lathe-bed, the string hanging vertically with a weight at lower end, damping of string is very small. Small changes in the configuration of the hanging weights (and so in end-conditions) make considerable differences in results.

(6) Using a very heavy single weight on the string, and keeping its disposition with respect to the string as constant as possible, it was found that k/n decreased with rising pitch, in contrast to the case of the wooden sonometer.

In connexion with the above, I wish to express my grateful thanks to Professor Morton, who suggested the subject of the investigation, and whose help and criticisms have been most valuable throughout; and to Mr. J. Wylie, who designed some special apparatus and whose suggestions on the experimental side have been most helpful.

LXV. *Some Experiments on the Vibration of Bars.* By E. F. RELF, A.R.C.Sc., and W. L. COWLEY, A.R.C.Sc., of the Aerodynamics Department, National Physical Laboratory*.

THE work described in this paper was undertaken in order to throw light on questions relating to the practical problem of vibration in aeroplane wing spars. Certain spars have been found to give marked vibration troubles through resonance with the engine or with aerodynamic forces over a wide range of frequency. For the sake of simplicity, investigation was confined to the case of a uniform thin beam symmetrically supported at three points. The spars used in aeroplane construction differ from this simple beam in two ways: (a) they are usually tapered, and (b) their depth is so great that the rotatory inertia of the beam elements might have an appreciable effect. These differences do not affect the general arguments of the present paper, but only their direct application to particular cases in practice.

The experiments were conducted upon a brass rod 0.126 in. diameter and 5.09 ft. long; full particulars of the method of experiment are given later in the paper. The frequencies of vibration in the fundamental and in several higher harmonics were calculated theoretically for the general case of a beam supported as in fig. 1, and the results were compared with those of experiment, using the value of E/ρ

Fig. 1.



found by a simpler experiment upon the same rod clamped at one end and free at the other.

It is evident, to begin with, that the frequencies will break up into two systems,—(A) the frequencies of one half of the beam formed by cutting at the centre support and clamping the end so formed, and (B) the frequencies of the same portion but with the clamp replaced by a simple support.

* Communicated by Mr. R. V. Southwell.

The results are given in figs. 2 and 3 in terms of the quantities ϕ_1 and ϕ_2 , respectively proportional to $l_1\sqrt{n}$ and $l_2\sqrt{n}$, where n is the frequency. Fig. 2 shows ϕ_2 plotted against ϕ_1 for the fundamental and the first four harmonics

Fig. 2.

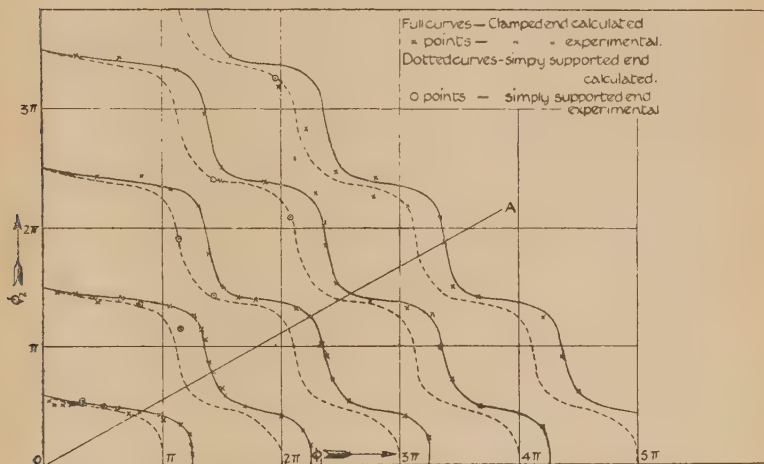
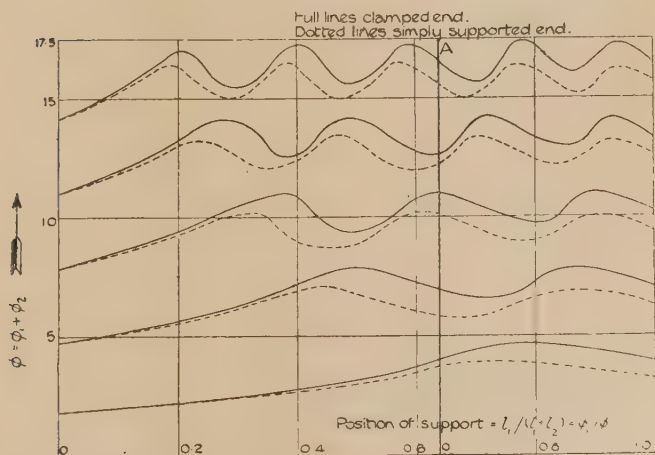


Fig. 3.



as the length ratio $l_1:l_2$ or $\phi_1:\phi_2$ is varied, while fig. 3 shows $\phi = \phi_1 + \phi_2$ plotted against $l_1/l_1 + l_2$ or ϕ_1/ϕ as abscissa.

Thus the square of the ordinate in fig. 3 is proportional to the resonance frequency. In fig. 2 the curves represent calculated values, the experimental results being indicated by crosses and circles, corresponding with full and dotted curves respectively. It will be seen that the agreement is excellent, except as regards the highest harmonic, where the speed of the forcing mechanism used in the experiments was very high, and general vibration impaired the accuracy of measurement. As a further comparison, the positions of the nodes in a particular case were determined and are given against the theoretical values in Table II.

The most interesting feature of the investigation is the tendency, shown in figs. 2 and 3, for the harmonics to group together in certain regions. Thus, a little to the right of the line OA in fig. 3, it will be seen that the first four harmonics occur over a comparatively small range of ϕ , whereas to the left of OA this range is almost doubled. In more complex structures this grouping effect may become even more marked, so that a particular structure may exhibit serious vibration over a considerable range of forcing frequency, whereas a slight modification of design might render it practically free of resonance over the same range.

Theoretical Investigation.

The case considered has already been described and is illustrated in fig. 1. The results have been expressed in non-dimensional form, so that they may be easily applied to all uniform beams symmetrically supported at three points.

The non-dimensional quantities used are :—

$$\left. \begin{aligned} \phi_1 &= l_1 \sqrt{\left\{ 2\pi n \sqrt{\frac{\rho}{EI}} \right\}} = l_1 \sqrt{\frac{2\pi n}{V_k}}, \\ \phi_2 &= l_2 \sqrt{\left\{ 2\pi n \sqrt{\frac{\rho}{EI}} \right\}} = l_2 \sqrt{\frac{2\pi n}{V_k}}, \end{aligned} \right\} \quad (1)$$

and $\phi = (l_1 + l_2) \sqrt{\left\{ 2\pi n \sqrt{\frac{\rho}{EI}} \right\}} = l \sqrt{\frac{2\pi n}{V_k}},$

where (see fig. 1)

l_1 is the distance of an outer support from the centre,
 l_2 is the length of the overhang,

$l = l_1 + l_2$, the half length of the beam,

n is the frequency of vibration,

ρ is the mass per unit length,

E is Young's modulus,

I is the moment of inertia of the cross-section about the neutral axis of the section,

k is the corresponding radius of gyration,

V is the velocity of sound along the rod.

The differential equation to be satisfied at every point of the beam (assuming the ordinary beam theory to hold, and neglecting rotatory inertia) is:—

$$\frac{\partial^4 y}{\partial x^4} + \frac{\rho}{EI} \frac{\partial^2 y}{\partial t^2} = 0, \quad \dots \dots (2)$$

which becomes, after writing $y \sin 2nt$ for y :—

$$\frac{\partial^4 y}{\partial x^4} - \lambda^4 y = 0, \quad \dots \dots (3)$$

where

$$\lambda^4 = 4\pi^2 n^2 \rho / EI = \phi^4 / l^4. \quad \dots \dots (4)$$

System (A). In this case the condition for resonance can be shown to be:—

$$\begin{aligned} & (1 - \cos \phi_1 \cosh \phi_1)(\sin \phi_2 \cosh \phi_2 - \cos \phi_2 \sinh \phi_2) \\ & = (1 + \cos \phi_2 \cosh \phi_2)(\sin \phi_1 \cosh \phi_1 - \cos \phi_1 \sinh \phi_1). \end{aligned} \quad (5)$$

If ϕ_1 and ϕ_2 are both large but not equal, a sufficient approximation is given by:—

$$\tan \phi_1 = 2 - \tan \phi_2. \quad \dots \dots (6)$$

The following special cases arise:—

- (1) If $l_1 = 0$ (beam clamped at one end and free at the other),

$$\begin{aligned} \cos \phi_2 &= -\operatorname{sech} \phi_2, \\ &= 0 \text{ for large values of } \phi_2; \end{aligned} \quad \dots \dots (7)$$

- (2) If $l_2 = 0$ (beam clamped at one end and simply supported at the other),

$$\begin{aligned} \tan \phi_1 &= \tanh \phi_1, \\ &= 1 \text{ for large values of } \phi_1. \end{aligned} \quad \dots \dots (8)$$

(3) If $l_1=l_2$, and therefore $\phi_1=\phi_2=\phi/2$,

$$\cos \phi = 0$$

$$\text{and } \tan \phi/2 = \tanh \phi/2,$$

$$= 1 \text{ for large values of } \phi. \quad \dots \quad (9)$$

System (B). In this case the condition of resonance becomes :—

$$\begin{aligned} (\sin \phi_1 \cosh \phi_1 - \cos \phi_1 \sinh \phi_1)(\sin \phi_2 \cosh \phi_2 - \cos \phi_2 \sinh \phi_2) \\ = 2 \sin \phi_1 \sinh \phi_1 (\cos \phi_2 \cosh \phi_2 + 1). \quad \dots \quad (10) \end{aligned}$$

If ϕ_1 and ϕ_2 are large, we have the approximation :—

$$\tan \phi_1 (\tan \phi_2 - 3) = \tan \phi_2 - 1.$$

The following special cases arise :—

$$(1) \text{ If } \phi_1 = 0, \quad \cos \phi_2 = -\operatorname{sech} \phi_2, \quad \dots \quad (11)$$

this being the same case as (7).

$$(2) \text{ If } \phi_2 = 0 \text{ (beam simply supported at both ends),} \\ \sin \phi_1 = 0 \text{ (excluding } \phi_1 = 0 \text{ as a solution).} \quad \dots \quad (12)$$

The equations (5), (6), (10), and (11) were conveniently solved by taking a series of values for ϕ_2 and deducing corresponding values of ϕ_1 , the approximate forms (6) and (11) being used when their accuracy was sufficient. The curves of figs. 2 and 3 were then plotted. From either set of curves the resonance frequencies for a given length-ratio l_1/l_2 can be found by drawing a straight line such as OA so that $\phi_1/\phi_2 = l_1/l_2$. Using fig. 2, the frequencies are given by

$$n = \frac{\phi_1^2}{l_1^2} \frac{Vk}{2\pi} = \frac{\phi_2^2}{l_2^2} \frac{Vk}{2\pi}, \quad \dots \quad (13)$$

while in fig. 3 the value of ϕ for abscissa $l_1/l = \phi_1/\phi$ gives

$$n = \frac{\phi^2}{l^2} \frac{Vk}{2\pi} = \left(\frac{\phi_1 + \phi_2}{l_1 + l_2} \right)^2 \frac{Vk}{2\pi}. \quad \dots \quad (14)$$

For large values of ϕ_1 and ϕ_2 the harmonics are separated from their neighbours by intervals of ϕ_1 and $\phi_2 = \pi$ nearly, as can be seen from the approximate forms (6) and (11). Also to a good approximation the separation is $\phi_1 = \pi$ when ϕ_1 is large and ϕ_2 small, and $\phi_2 = \pi$ when ϕ_2 is large and ϕ_1 small.

The calculated values are given in Table III. for case (A) and in Table IV. for case (B), only the fundamentals and

first harmonics being tabulated. Higher harmonics may be obtained by increasing ϕ_1 or ϕ_2 by π , 2π , 3π , etc., keeping ϕ_2 or ϕ_1 respectively constant.

In figs. 2 and 3 the full curves apply to case (A) and the dotted curves to case (B), both systems together giving the solution for the complete beam.

Experimental Verification.

The brass rod used in the experiments was held in some cases vertically and in others horizontally. At one end the support consisted of an oscillating lever to which the rod was clamped for case (A), and attached by a ball joint for case (B). This lever was connected to an eccentric driven by a small electric motor whose speed could be varied in order to apply forced vibrations of any required frequency to the end of the rod. The movement at the support was of the order of 0.01 inch. The second support for the rod consisted of a slotted steel strip, the slot being bevelled so as not to produce any constraint upon the rod other than that required by a simple support. The position of this support along the rod was varied so as to give a series of values to the length ratio l_1/l_2 .

As the speed of the motor was gradually increased, positions were reached at which marked resonance occurred, the nodes and loops along the rod being clearly seen. These speeds were measured by means of a revolution counter and stop-watch. The fundamental period was too slow for the motor, and was determined by timing the free swings of the rod.

Comparison between Theory and Experiment.

Before the experimental results can be compared directly with theory the value of V , the velocity of sound along the rod, must be known. To determine this quantity the movable support was taken away and the rod hung vertically, clamped to the forcing lever. The resonance frequencies were then determined and the corresponding values of ϕ calculated from (7). This led to the results given in Table I.

The ratios ϕ^2/n are constant except at the two lowest frequencies, where the pendulum effect is modifying the results.

TABLE I.

ϕ	1.87	4.69	7.85	10.99	14.15
n	0.808	4.22	11.4	22.1	36.7
ϕ^2/n	4.33	5.23	5.42	5.46	5.45

Using the highest frequency, we have $\phi = \lambda l = 14.15$ for $n = 36.7$, and inserting the rod dimensions $l = 5.09$ feet and $k = 0.0315$ inch, we find that

$$V = \frac{2\pi n}{\lambda^2 k} = 11,370 \text{ ft./sec.}$$

This value was accordingly used in the further experiments to obtain ϕ from n , the observed frequency.

The positions of the nodes were observed in the simple case of the rod with one end clamped and the other free. They are tabulated below, together with the theoretical values given in Lord Rayleigh's 'Theory of Sound,' and it will be seen that the agreement is excellent.

TABLE II.

Distances of Nodes from Clamped End, expressed as fractions of the length of the rod.

2nd Harmonic	Theory	0.868	0.500	—	—
		Experiment	0.868	0.505	—	—
3rd Harmonic	Theory	0.906	0.644	0.356	—
		Experiment	0.905	0.633	0.354	—
4th Harmonic	Theory	0.927	0.723	0.500	0.278
		Experiment	0.927	0.722	0.508	0.262

TABLE III.

One end clamped and a simple support elsewhere.

(a) Fundamental Curve.

ϕ_1	3.93	3.93	3.91	3.85	3.70	3.28	2.5	2.22
ϕ_2	0	0.25	0.5	0.75	1.0	1.25	1.44	1.5
ϕ	3.93	4.18	4.41	4.60	4.70	4.53	3.94	3.72
ϕ_1	2.0	1.57	1.5	1.0	0.5	0.25	0	
ϕ_2	1.51	1.57	1.58	1.67	1.74	1.82	1.84	
ϕ	3.51	3.14	3.08	2.67	2.24	2.07	1.84	

(b) 1st Harmonic.

ϕ_1	7.07	7.07	7.06	6.99	6.85	6.48	5.57
ϕ_2	0	0.25	0.50	0.75	1.00	1.25	1.50
ϕ	7.07	7.32	7.56	7.74	7.85	7.73	7.07
ϕ_1	4.89	4.63	4.50	4.42	4.36	4.31	4.25
ϕ_2	1.75	2.00	2.25	2.50	2.75	3.0	3.25
ϕ	6.64	6.63	6.75	6.92	7.11	7.31	7.50
ϕ_1	4.18	4.11	4.00	3.93	3.50	3.83	3.0
ϕ_2	3.50	3.75	3.86	3.93	4.16	4.00	4.26
ϕ	7.68	7.86	7.86	7.86	7.66	7.83	7.26
ϕ_1	2.5	2.0	1.5	1.0	0.5	0.25	0
ϕ_2	4.33	4.40	4.46	4.53	4.62	4.64	4.71
ϕ	6.83	6.40	5.96	5.50	5.12	4.89	4.71

TABLE IV.

Simple support at one end and another elsewhere.

(a) Fundamental.

ϕ_1	3.14	3.13	2.93	2.66	2.02	1.55	1.08	0.76	0.57	0
ϕ_2	0	0.50	1.0	1.2	1.4	1.5	1.6	1.7	1.8	1.84
ϕ	3.14	3.63	3.93	3.86	3.42	3.05	2.68	2.46	2.37	1.84

(b) 1st Harmonic.

ϕ_1	6.28	6.27	5.80	5.19	4.17	3.82	3.62
ϕ_2	0	0.50	1.0	1.4	1.7	2.0	2.5
ϕ	6.28	6.77	6.80	6.59	5.87	5.82	6.12
ϕ_1	3.50	3.38	3.05	2.53	1.32	0.60	0
ϕ_2	3.0	3.5	4.0	4.2	4.4	4.6	4.71
ϕ	6.50	6.88	7.05	6.73	5.72	5.20	4.71

TABLE V.—Clamped end.

Values of ϕ_1 (Experimental).

Length ratio $l_1/l_2 = \phi_1/\phi_2$.	Fundamental.	Harmonics.			
		1st.	2nd.	3rd.	4th.
0.085	0.143	0.384	0.66	0.93	1.18
0.180	0.289	0.810	1.37	1.94	2.49
0.334	0.537	1.44	2.56	3.50	4.16
0.456	0.756	2.02	3.34	4.25	4.44
0.593	0.96	2.56	4.05	4.67	—
0.617	—	—	—	4.74	6.20
0.774	1.232	2.27	4.33	5.80	6.90
1.0	1.58	3.97	4.70	7.18	7.74
1.152	—	4.18	5.16	7.40	8.80
1.224	—	—	—	—	8.74
1.280	1.95	4.26	5.60	7.43	—
1.402	—	—	—	—	9.64
1.600	2.21	4.37	6.66	7.71	10.5
1.788	2.52	4.47	7.09	8.18	10.6
2.28	3.06	4.74	7.36	9.60	10.8
2.58	3.18	4.80	7.50	10.28	11.5
3.36	3.60	5.33	7.63	10.5	13.2
4.72	3.83	6.28	8.06	10.8	13.7
7.28	3.81	6.84	9.55	11.5	14.1
13.13	3.90	7.09	10.22	13.2	16.1
23.6	—	—	—	13.4	16.5

TABLE VI.—Simply supported end.

Values of ϕ_1 (Experimental).

Length ratio $l_1/l_2 = \phi_1/\phi_2$.	Fundamental.	Harmonics.			
		1st.	2nd.	3rd.	4th.
0.6	1.05	2.56	3.60	4.53	6.17
1.0	1.62	3.60	4.50	6.54	—

LXVI. *The Crystal Structure of Cuprite and Rutile.* By
GILBERT GREENWOOD, M.Sc., *John Harling Fellow in the*
University of Manchester *.

PREVIOUS investigations of both these minerals have been carried out by means of X-rays, and the published accounts would suggest that they are worthy of further investigation. Cuprite is an example of those interesting cases where the symmetry as deduced crystallographically from geometrical considerations is at variance with that assigned to the crystal from an investigation of its structure. The structure described by W. H. and W. L. Bragg ('X-rays and Crystal Structure,' 1924, p. 147) is cubic holohedral, whilst the undoubted holoaxial character of certain crystals is shown by the {986} face, found by H. A. Miers (Phil. Mag. xviii. p. 127, 1884). The position with regard to rutile, which crystallizes in the tetragonal system, is slightly different: the divergence of opinion in this case is as to the correctness of two different proposed structures. Rutile has been investigated by Vegard (Phil. Mag. xxxii. p. 65, 1916) and also by Williams (Proc. Roy. Soc. xciii. A, p. 418, 1917). They both obtained somewhat similar spacings, but Williams found, in addition, two new reflexions occurring at half the first order glancing angles determined by Vegard for the (100) and (111) planes: he also obtained different values for the intensities of the spectra.

The investigation of these minerals now to be described was carried out by the X-ray spectrometric method, the radiation used being the $K\alpha$ rhodium rays of wave-length 0.615 Å. Attention was particularly concentrated on the measurement of intensities rather than on the accurate determination of glancing angles. The measurement was made in the following manner. A comparatively wide chamber slit was used and a series of readings were made over a range which includes the peak. To make a reading the crystal was swept with a uniform angular velocity through the reflecting angle corresponding to the chamber setting. The total ionization produced in the chamber was measured by adjusting the potential so that the electrometer string returned to zero. This applied potential is then a measure of the quantity of X-rays received in the chamber. On plotting the intensity values thus obtained against the chamber angles a flat-topped peak of the type depicted by

* Communicated by Professor W. L. Bragg, F.R.S.

Bragg, James, and Bosanquet (Phil. Mag. xli. p. 309, 1921) is obtained. From a graph of this type it is very easy to obtain a true measurement of the reflexion alone as distinct from the general radiation. In order to express each reflexion on a common scale, so that they would all be strictly comparable, they were compared directly with the second order reflexion from the (100) planes of rocksalt, measured at once, under the same conditions, and in the same manner. The faces of both the minerals and the rock-salt were large enough to intercept the whole of the incident beam. The error introduced by unequal absorption, due to incorrectly ground faces, was eliminated by making one reading with the crystal reflecting to the right-hand side, and then turning it round so as to reflect to the left-hand side and making a second reading. The mean of these two has been shown by W. H. Bragg (Phil. Mag. xxvii. p. 888, 1914) to be the real intensity of the reflected beam. All the intensities are expressed as percentages of the 200 reflexion from rocksalt. Owing to the "extinction factor" effect in measuring particular intensities, the doubt as to the relative scattering powers of the atoms etc., it will be better to seek for an atomic arrangement which gives the best general agreement rather than to try to find an arrangement which gives quantitative agreement for one or two orders. See W. L. Bragg (Proc. Roy. Soc. cv. A, p. 34, 1924).

CUPRITE.

The results of the measurements made as described above are set out in the following table. The glancing angle for the first order for each face is a mean value obtained from the crystal and chamber settings for all the orders measured on both the right- and left-hand sides. The other values which are given in the first column, and refer to orders higher than the first, have been calculated from the glancing angle.

TABLE I.

Angle.	Sin.	hkl .	I.	log I.	A.	$\frac{I}{A}$.	$\frac{I}{A^2}$.
$5^{\circ} 49'$	0.1014	110	7.2	0.8573	8	0.9	0.0112
$7^{\circ} 8'$	0.1242	111	185.5	2.2684	58	3.2	0.055
$8^{\circ} 15'$	0.1435	100	110.0	2.0414	50	2.2	0.033
$11^{\circ} 42'$	0.2028	220	61.9	1.7914	66	0.94	0.014
$14^{\circ} 23'$	0.2484	222	26.0	1.4150	50	0.52	0.010
$16^{\circ} 41'$	0.2870	200	18.5	1.2672	66	0.28	0.0043
$17^{\circ} 43'$	0.3042	330	—	—	8	—	—
$21^{\circ} 52'$	0.3726	333	8.5	0.9294	58	0.147	0.0025
$23^{\circ} 56'$	0.4056	440	7.0	0.8451	66	0.106	0.0016
$25^{\circ} 30'$	0.4305	300	3.7	0.5682	50	0.074	0.0015

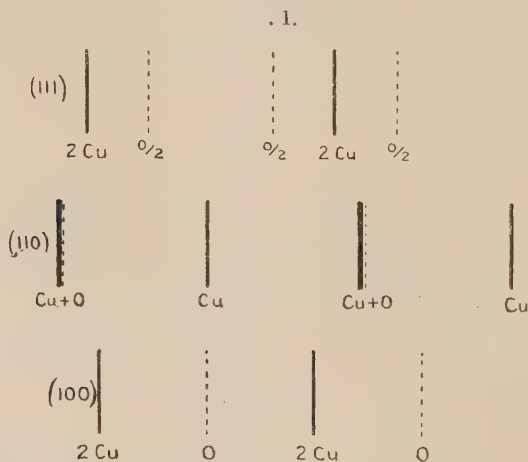
Calculation shows that $d_{100} = 2.142 \text{ \AA}$, and that the volume d_{100}^3 contains one quarter of a molecule, *i.e.* two molecules in the larger cube of edge $2d_{100}$. This is in agreement with the structure previously found. In this structure the copper atoms lie on a face-centred cubic lattice and the oxygen atoms on a centred cubic lattice of the same dimensions. The oxygen lattice is displaced with respect to the copper lattice in the direction of one of its diagonals for a distance equal to one quarter of the diagonal length. In addition, the small first order reflexion from the (110) planes which had been overlooked in the earlier investigation (see 'X-rays and Crystal Structure,' 1924, p. 145, fig. 53) has now been found. The spacings of the planes are given in fig. 1 and the structure factors by the equation :

$$A_{100} = 58 + 8 \cos n \pi,$$

$$A_{111} = 58 + 8 \cos n \frac{\pi}{2},$$

$$A_{110} = 37 + 29 \cos n \pi,$$

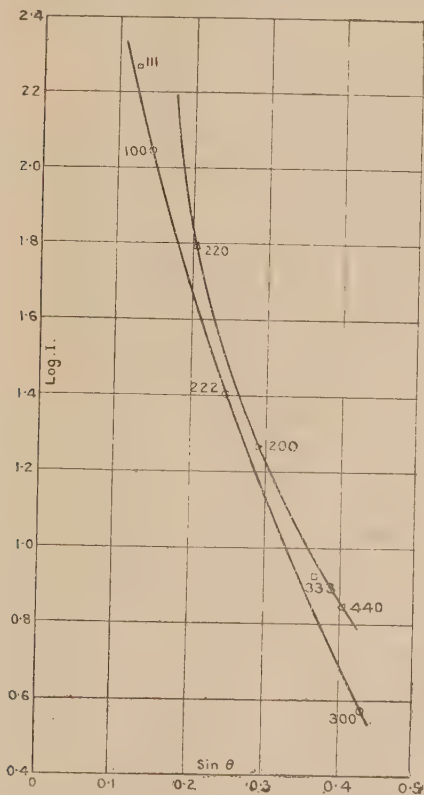
where n is the order of the spectrum.



The "weight" of a diffracting centre was taken as proportional to its atomic number—29 for Cu and 8 for O. From a consideration of these structure-factors we find that the reflexions can be divided into four groups:—200, 220, and 440, with a factor of 66; 111 and 333, with a factor of 58; 100, 300, and 222, with a factor of 50; and finally 110 and 330, with factors of 8.

It is easy to see that the 110 and 330 reflexions are in agreement with the above: 110 was quite small, and 330 was too small to observe even though 440 was fairly big. It is, however, much more difficult to find even a general agreement among the other spectra, since the factors are all so nearly equal. Fig. 2, in which the logarithm of the intensity is

Fig. 2



plotted against the sine of the angle of reflexion, shows that this agreement does undoubtedly exist. Reflexions 100, 300, and 222 fall on the lower curve and reflexions 200, 220, and 440 on the upper curve, whilst 111 and 333 lie in between these two curves. It is always of interest to see whether the measured intensities appear to vary as the structure-factor or as its square. Theoretically they might be expected to vary as the square, and this has been found to be the case with some simple structures such as rocksalt. On the other hand, in more complicated structures such as

calcite and aragonite the intensities have been found to vary more nearly as the first power of the factor. In the last two columns of Table I. are given the values of $\frac{I}{A}$ and $\frac{I}{A^2}$.

On plotting these values against the corresponding angle, either set of points fits about equally well on a smooth curve. A reason for this indifference of choice between the structure-factor or its square may possibly be found in the fact that all the factors concerned have very nearly their maximum value.

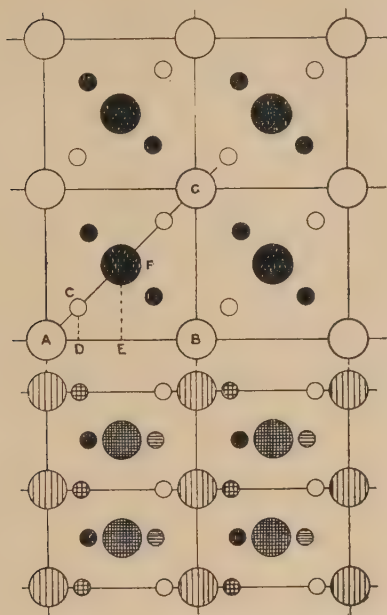
RUTILE.

The results obtained in this investigation leave no doubt as to the correctness of Vegard's earlier work. A careful search for the two reflexions described by Williams entirely failed to reveal any trace of them. The result of the intensity measurements was a slight alteration of the one parameter involved in the structure proposed by Vegard. The measurement of the spacing of the (100) planes gave $d_{100} = 2.29 \text{ \AA}$, which is in satisfactory agreement with Vegard's value of 2.26 \AA . Further determinations of glancing angles were not made, the angles found by Vegard being used throughout the work. Calculation shows that a quarter of a molecule is contained in the cell $d_{100}^2 \times d_{001}$, and this suggested that the type of structure was that of a centred prism. This is in agreement with the type of structure deduced by Vegard, which is illustrated in fig. 3. The upper part of the figure is a projection on the plane (001), whilst the lower portion of the figure shows a projection on the plane (100). The large circles represent titanium atoms and the small ones oxygen; circles differently shaded lie in different planes.

The titanium atoms lie on a centred tetragonal lattice, whilst the oxygen atoms are on four simple tetragonal lattices, interpenetrating the titanium lattice in the manner shown in the drawing. The (001) planes contain both oxygens and titaniums, each plane of this series is a repetition of any other one.

If we consider the titanium atoms on a centred tetragonal prism of edges $2d_{100}$, $2d_{100}$, and $2d_{001}$, we find that it will give spacings for the (100), (110), (101), and (001) planes, which agree with those experimentally found. The spacing for (111) was found to be twice as great as would have been expected. As will be seen later, this is due to the oxygen atoms: the titanium planes parallel to (111) alternately do and do not contain oxygen atoms in addition to the titanium. Hence the spacing is twice the distance between adjacent (111) planes of a centred tetragonal lattice of titanium atoms.

Fig. 3,



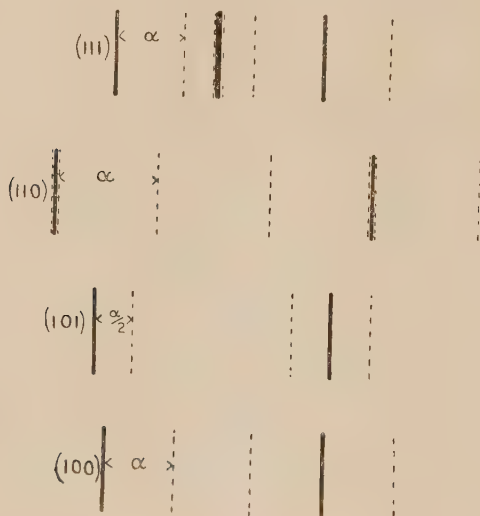
The following Table shows the experimental results :—

TABLE II.

Angle.	Sin.	hkl .	I.	A.	A^2 .	$\frac{I}{A}$.	$\frac{I}{A^2}$.
$5^\circ 26'$	0.0947	110	278	24.4	586	11.48	0.474
$7^\circ 4'$	0.1231	101	95.2	16.1	259	5.92	0.404
$7^\circ 41'$	0.1337	100	41.1	10.4	108	3.99	0.380
$8^\circ 5'$	0.1406	111	59.6	13.8	191	4.32	0.312
$10^\circ 55'$	0.1894	220	105	35.6	1268	2.95	0.083
$11^\circ 57'$	0.2071	001	104	38	1442	2.74	0.072
$14^\circ 14'$	0.2459	202	10	10.3	103	0.98	0.098
$15^\circ 31'$	0.2675	200	27	23.1	533	1.17	0.051
$16^\circ 20'$	0.2813	330	40	30.5	935	1.32	0.043
$16^\circ 30'$	0.2840	222	38	35	1228	1.09	0.031
$21^\circ 40'$	0.3692	303	19.6	36.4	1324	0.54	0.015
$22^\circ 18'$	0.3795	440	6.7	22.1	489	0.303	0.0138
$23^\circ 29'$	0.3985	300	10	32.5	1030	0.307	0.0097
$24^\circ 28'$	0.4142	002	18	38	1442	0.473	0.0125
$25^\circ 0'$	0.4226	333	—	2.7	7.6	—	—
$28^\circ 15'$	0.4734	550	7	36.6	1340	0.193	0.0052
$29^\circ 22'$	0.4904	404	3.7	23.1	533	0.160	0.0069
$32^\circ 20'$	0.5349	400	1.8	6.1	38.2	0.295	0.0472
$34^\circ 15'$	0.5628	444	2	22.1	489	0.090	0.004
$38^\circ 25'$	0.6213	003	3.6	38	1442	0.095	0.0025

The results are of a similar order to those of Vegard, but though the actual values are somewhat different the arguments in favour of a structure on pp. 77-81 of his paper (*loc. cit.*) are still quite valid. The side of the unit cell is $AB = a = 2d_{100}$. The position of the oxygen atoms—say C—

Fig. 4.



is fixed by a parameter ϵ (a fraction of a), the length AD being ϵa . The spacings for the various planes are shown in fig. 4, and the corresponding structure-factors are given by

$$\left. \begin{aligned} A_{100} &= 22 + 16 \cos n\alpha, \\ A_{110} &= 30 + 8 \cos n\alpha, \\ A_{101} &= 22 + 16 \cos n\frac{\alpha}{2}, \\ A_{111} &= \frac{1}{2} [22 + 16 \cos n\alpha + 38 \cos n\pi]. \end{aligned} \right\} \quad \cdot \cdot (1)$$

The connexion between ϵ and α is $\epsilon = \frac{AD}{AB} = \frac{AD}{2AE} = \frac{\alpha}{4\pi}$.

The "weight" given to the titanium atoms was 22.

The value of ϵ was determined thus:—From the proposed structure it will be seen that the (001) planes would give a normal sequence of spectra. This is borne out by the measured intensities of the first three orders, which are very

similar to those from (100) of rocksalt—a well-known normal sequence. The intensities of all the orders were now plotted against their corresponding angle and a curve drawn through (001), (002), and (003): this gives the normal decrease of intensity with angle. All the other intensities which lie on the graph below this normal curve were expressed as a fraction of the corresponding normal value for that angle. The reflexions were then arranged in a descending series of their fractional sizes. When the true value of ϵ has been chosen, the calculated structure-factors should also be in this same order. As previously stated, our object was to choose a value for ϵ which gives the best general agreement: the method adopted was very similar to that of A. J. Bradley (Phil. Mag. xlvii. p. 657, 1924). It is very easy by the construction of a few graphs to solve the equations (1) for any value of $\frac{\alpha}{2}$. Solutions were obtained for various angles,

and the resulting structure-factors arranged in descending order and compared with the experimentally determined descending series of intensities. The mean error in each case was determined. It showed a well-marked minimum for a certain angle. The results obtained are given in the table.

TABLE III.

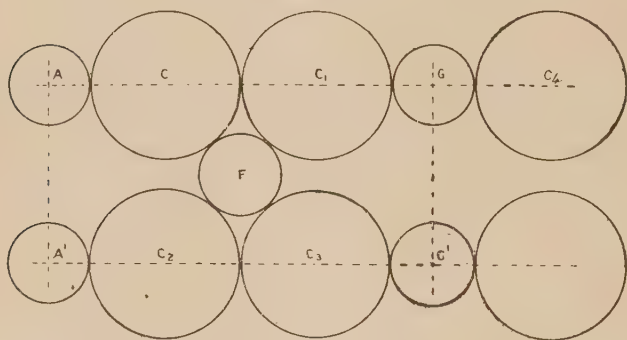
$\frac{\alpha}{2}$	Error.	$\frac{\alpha}{2}$	Error.
100°	3.41	110°	1.65
104°	2.12	112°	1.83
106°	2.0	120°	2.59
108°	1.47		

The value of α is therefore 216°, and this makes $\epsilon=0.300$. If, now, l is the length AC of fig. 3, *i. e.* the distance between oxygen and titanium centres, the value of l works out to be 1.948 Å.

The packing together of the atoms in space must now be considered. In consultation with Professor W. L. Bragg it was decided to attempt to make the spheres, of which structural models are usually built up, of such a size as to represent, more or less, the diameter of electronic orbits of the atoms concerned. From this point of view the metallic element atoms would be smaller than those of the non-metals, not *vice versa* as has been often used in the construction of such models. In the case of rutile the most important

plane is (110), or the line ACFG of fig. 3. The points A, A', G, G', C, C₁, C₂, C₃, and F of fig. 5 are already fixed as the centres of atoms. As was pointed out by Niggli (*Zeit. für Krist.* lvi. p. 119, 1921) and Jertsch (*Zeit. für Krist.* lviii. p. 293, 1923) in Vegard's original structure, the distances from the oxygen atom C to the two titanium atoms A and F were different, even though the atoms must touch along these two directions, in order to hold the structure together. Owing to the change in the parameter ϵ this peculiarity has now disappeared. Calculation shows that $AC=1.95 \text{ \AA}$ and $CF=1.96 \text{ \AA}$ —a difference of 0.01 \AA instead of, as originally, 0.1 \AA . Thus, giving the oxygens their largest size, we obtain the length $CC=2.58 \text{ \AA}$ as the diameter. The titanium

Fig. 5.

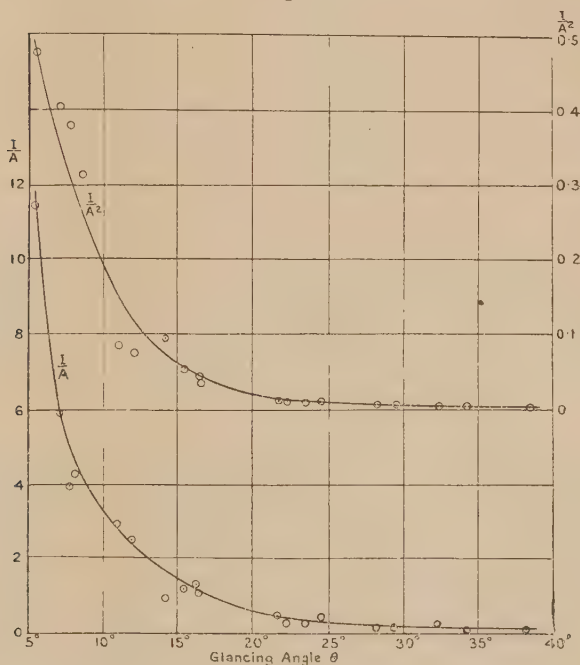


atoms which fit in between the four oxygens C C₁ C₂ C₃ and in between the two oxygens C₁ and C₄, then possess a diameter of 1.32 \AA . The value 2.58 \AA for oxygen is a maximum: it would still be possible to fit the structure together using smaller oxygens and correspondingly larger titaniums. It is again of interest to see whether the measured intensities vary as the square of the amplitude-factor or as the amplitude-factor itself.

In columns 7 and 8 of Table II. are recorded the values of $\frac{I}{A}$ and $\frac{I}{A^2}$. Fig. 6 shows these values plotted against the corresponding angles. An inspection of the curves shows that in the case of smaller angles the $\frac{I}{A}$ graph is more satisfactory, whilst for larger angles the reverse is true. It

has been found before (see W. H. Bragg, Proc. Phys. Soc. Lond. xxxii. pt. 5, Aug. 1921) that for the larger reflexions the "extinction" factor has a greater influence, decreasing them more than it does the smaller spectra. When this occurs the intensities become more proportional to the structure-factor itself than to its square. Since the greater reflexions occur at the smaller glancing angles, one would expect to find the spectra at these smaller angles varying more as the factor itself. This is what occurs with rutile.

Fig. 6.



Finally I wish to express my indebtedness to Professor W. L. Bragg and Mr. R. W. James for their helpful advice during the course of the work, and also to Miss Lucy Wilson, of Wellesley College, for assistance in the calculations of structure-factors and intensities.

LXVII. *A New Determination of the Constant N of Avogadro, based on its Definition.* By PIERRE LECOMTE DU NOÛY, D.Sc.*

[From the Laboratories of the Rockefeller Institute for Medical Research, New York.]

[Plate XIII.]

IT has been shown in a previous paper† that it was possible to obtain monomolecular layers of certain colloidal substances, such as sodium oleate, and the technique and instrument used to establish the criterion of the existence of such a layer have been described. It is therefore unnecessary to repeat a description of the experimental work, which has also been dealt with in great detail in the 'Journal of General Physiology'‡ and 'Journal of Experimental Medicine'§.

Subsequent to the writing of the last paper, further experiments were made with pure sodium oleate, especially prepared in this laboratory by Dr. L. Baker; investigations with higher dilutions revealed two other minima of the surface tension at $1/1,390,000$ and at $1/1,220,000$. The purpose of this paper is to explain these new minima, and to apply the data yielded to a determination of the fundamental constant N.

I.

The apparatus used is shown in Pl. XIII. Series of 24 different dilutions at a time were placed in the standard watch-glasses, in which the total surface of adsorption was 26.4 sq. cm. (diameter of the free surface of the liquid = 4.08 cm., area = 13.08 sq. cm.; maximum depth at the centre = 0.3 cm.; surface of the glass, segment of sphere, 13.33 sq. cm.). Each watch-glass was placed on a bronze ring, levelled by means of three levelling-screws, which could therefore be raised parallel to itself, without jarring, in order to bring the surface of the solution in contact with the ring of the tensiometer. The results of ten series of measurements are given in Table I. Some of the experiments are plotted in Charts I., II., and III.

* Communicated by the Author.

† du Noüy, P. L., *Phil. Mag.* xlviii. p. 264 (1924).

‡ du Noüy, P. L., *Journ. Gen. Phys.* i. no. 5, p. 521 (1919), and July 1924 (vol. vi. p. 625).

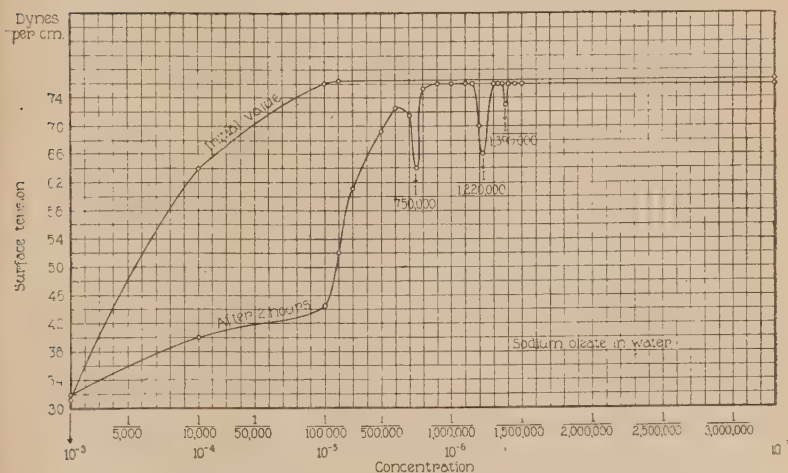
§ du Noüy, P. L., *Journ. Exp. Med.* xxxv. pp. 575 707 (1922), xxxviii. p. 87 (1923).

TABLE I.

Concentrations at which the 3 minima occurred in 10 series of experiments, in the value of the surface tension of sodium oleate solutions, after 2 hours' standing.

No. of experiment.	First minimum. C_1 .	Second minimum. C_2 .	Third minimum. C_3 .
1	1/750,000	1/1,220,000	1/1,390,000
2	1/750,000	1/1,220,000	1/1,390,000
3	1/749,000	1/1,220,000	1/1,380,000 (?)
4	1/750,000	1/1,222,000	1/1,391,000
5	1/749,000	1/1,220,000	1/1,390,000
6	1/751,000	1/1,222,000	1/1,390,000
7	1/751,000	1/1,222,000	1/1,395,000
8	1/750,000	1/1,220,000	1/1,386,000
9	1/750,000	1/1,218,000	1/1,390,000
10	1/750,000	1/1,221,000	1/1,390,000

Fig. 1.



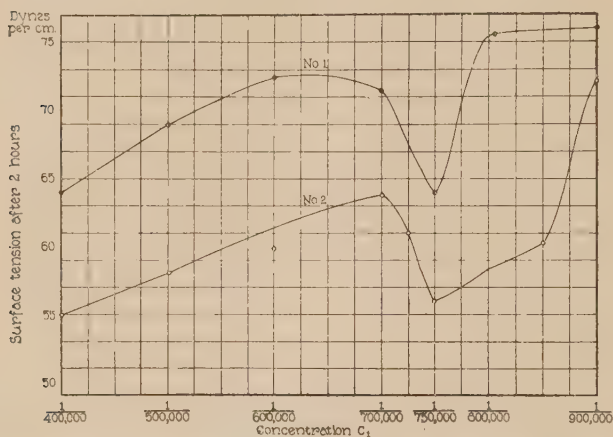
Surface tension of sodium oleate in water, after two hours, in function of the concentration.

Three decided minima, always occurring at the same concentrations, are observed: one at 1/750,000, the second at 1/1,220,000, and the third at 1/1,390,000.

As a rule, all minima in good experiments occurring exactly at the concentrations 1/750,000, 1/1,220,000, and

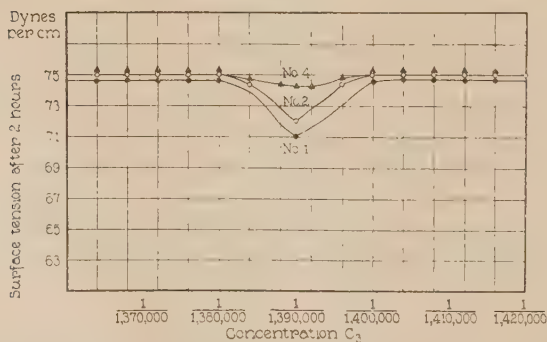
1/1,390,000 are always more marked and larger in absolute value than those occurring at other concentrations near by. No important and well-defined minimum was ever observed, except at these concentrations. It seems that when a displacement occurs it is due either to an experimental

Fig. 2.



Surface tension of sodium oleate in water, after two hours, in function of the concentration.

Fig. 3.



Surface tension of sodium oleate in water, after two hours, in function of the concentration.

accident, or to the impossibility of the molecules to organize themselves so as to produce the minimum field of forces. In such a case the place of the minimum does not mean anything. For this reason, the writer does not believe that a mean value would express the truth more accurately

than can be done by choosing as critical concentrations those at which the minima are more sharply defined and more important in absolute value.

I have pointed out in my previous paper that the minimum at 1/750,000 corresponds probably to the existence of a monolayer of vertically organized molecules. The calculation yielded a figure close enough to the length assumed by Langmuir for the molecule of oleic acid * to support this view. In the present set of experiments, greater care was taken with the measurement of the total area of the liquid in the watch-glasses, and it was found that the total surface was 26.41 sq. cm. instead of 25.6, as introduced in our first calculations. This error being corrected, the length of the molecule of sodium oleate is now 12.30×10^{-8} cm., assuming that all the molecules are adsorbed. This assumption is a natural and logical consequence of the fact that the length of the molecule of oleic acid is 11.2×10^{-8} cm.; as the Na atom replaces one H atom at the end of the molecule, it is very probable that the length is increased slightly. Should only 10 per cent. of the molecules be free in the solution, then the quantity of substance adsorbed would be smaller, and the length of the molecule would be 11.2×10^{-8} cm. In other words, there would be no change in the length of the molecule of oleic acid after substitution of H by Na. This does not agree with the actual chemical conception of this molecule. Therefore we shall provisionally admit that the molecules are all adsorbed, and that 12.30×10^{-8} cm. corresponds to the length of the molecule of sodium oleate. The increase of length due to the Na atom is then 1.1×10^{-8} cm. (Of course, this represents the projection on the longitudinal axis of the molecule, and not the real distance from the Na atom to the O atom, to which it is linked.)

Let us now consider the second minimum. The same calculation ($1/1,220,000 \times 2 =$ amount of substance in the watch-glass, divided by the area 26.4, gives the amount per sq. cm. This figure is in turn divided by the specific gravity) yields the thickness of the layer. It is 7.56×10^{-8} cm. This minimum can only occur if a critical organization of molecules takes place. Consequently, in this case, we have another monolayer, but the molecules are horizontally arranged, and 7.56×10^{-8} cm. is one of the dimensions of the base of the molecule.

The third minimum, at 1/1,390,000, corresponds to a third monolayer, the thickness of which is 6.64×10^{-8} cm.

* R. A. Millikan, J. Am. Chem. Soc. xxxix. (1917).

This is the third dimension of the molecule, which, at this dilution, lies flat on the surface, occupying a rectangular area 7.56×12.30 sq. cm. $\times 10^{-16}$. [In the second position (at a dilution of $1/1,220,000$) it occupies, in the horizontal plane, an area equal to 6.64×12.30 sq. cm. $\times 10^{-16}$, and in the first position (vertical molecules, at a dilution of $1/750,000$) it occupies in the horizontal plane an area equal to 7.56×6.64 sq. cm. $\times 10^{-16}$.] This may be true, regardless of the real shape of the molecule, since we are only concerned with the space occupied by one molecule when symmetrically packed with others.

These three dimensions make it possible now to compute the volume of the molecule, and, knowing the specific weight of the substance (0.821), its mass in grams is found to be 507×10^{-24} gram. By dividing the molecular weight of sodium oleate (304.35) by the mass of one molecule, according to the very definition, we obtain the constant N:

$$N = 6.003 \times 10^{23}.$$

This value agrees within 0.1 per cent. with the value found by Millikan (6.062×10^{23}), which he considers as correct within ± 0.006 †.

From this value of N, one obtains readily the value of the electron (4.82×10^{-10} U.E.S.) and that of the mass of the hydrogen atom (1.677×10^{-24} gram). (Instead of 4.77×10^{-10} and 1.662×10^{-24} by Millikan.)

This accord is quite remarkable, considering the extreme simplicity and directness of the method and of the calculation based only on the definition of Avogadro. However, an objection may be raised as to the number of molecules adsorbed. In other words, does the number of organized adsorbed molecules actually correspond in the three different experiments (at three different concentrations) to the actual number of molecules in solution? This can be checked three times, once for every concentration, each control being absolutely independent of the other, as the three dimensions are obtained from three different experiments. So that, should the figures coincide in every case, their correctness will have been proven three times independently.

First control.—Concentration $1/750,000$. The problem can be stated in the following way:—It is assumed that the horizontal space occupied by one single vertical molecule is

† R. A. Millikan, 'The Electron' (University Chicago Press, 1917).

$7.56 \times 6.64 = 50.2 \times 10^{-16}$ sq. cm. At a given dilution, namely 1/750,000, it is assumed that they are all adsorbed on the free surface of the liquid + the surface of the glass. Consequently, as the total number of molecules present in the solution can be calculated (by dividing the mass of substance in solution by the mass of one molecule), the product—number of molecules \times area of one molecule—should be near the value of the total area of adsorption, namely 26.41 sq. cm.

We have in solution 5.26×10^{15} molecules; the area of a single molecule is 50.2×10^{-16} . The product is 26.4 sq. cm., identical with the surface of adsorption.

Second control.—Concentration 1/1,220,000. Here we have, according to the same calculation, 3.232×10^{15} molecules in the solution. The space occupied by the tilted horizontal molecule is $6.64 \times 12.30 = 81.7 \times 10^{-16}$ sq. cm. The product is

$$(81.7 \times 10^{-16}) \times (3.232 \times 10^{15}) = 26.4 \text{ sq. cm.}$$

Third control.—Concentration 1/1,390,000. In this case the molecules lie flat, occupying an area $7.56 \times 12.30 = 93.0 \times 10^{-16}$ sq. cm. We have 2.838×10^{15} molecules in solution. The product is

$$(93.0 \times 10^{-16}) \times (2.838 \times 10^{15}) = 26.4 \text{ sq. cm.}$$

In the three cases the figures check to the first decimal point.

It is not unnecessary to remark that there is no fallacy whatever in the foregoing reasoning. Each dimension is obtained from a separate set of experiments at a given dilution. This dimension—thickness of the layer of adsorbed molecules—is obtained from the known weight of substance present, assumed to be spread evenly on the total surface of adsorption. The thickness of two such layers (at two different critical concentrations) is then carried to the third experiment, and assumed to be the horizontal dimension of the individual molecule.

Discussion and Evaluation of Errors.

The errors involved in this method are small, because, with the exception of the determination of weights, volumes, and surface of adsorption, which can be performed with a

good degree of accuracy, no quantitative measurements of the surface tension are required. The whole computation depends on the determination of a minimum value of the surface tension of solutions after two hours' standing. Although these determinations require great care, they are remarkably constant, and the minima are sharply defined (Charts I., II., III., and Table I.).

If it be admitted that the molecular weight of sodium oleate is exact, or if we choose to neglect the possible error—which is certainly very small—in the atomic weights of its constituents, it may be stated that the error in the value of N is dependent solely on the errors involved in the determination of the mass of one single molecule of sodium oleate. This mass, as calculated from our measurements, may be expressed by the formula

$$M = \frac{m^3 \cdot C_1 \cdot C_2 \cdot C_3}{A^3 \cdot \delta^2}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

as one of the linear dimensions is equal to

$$L = \frac{m \cdot C}{A \cdot \delta}.$$

M = mass of one molecule of substance (to be computed).

m = mass of mixture in watch-glass, always assumed, at $22^\circ\text{C.} = 2 \times 0.9979$ (temperature correction). This is true if density of water is 1 gr./cm.^3 , and the concentration of the substance very small.

A = area of adsorbing surface (total surface of water in contact with air and glass).

δ = specific gravity of substance in solution.

C_1, C_2, C_3 = critical concentrations at which the minima are observed.

The various values of the critical concentrations C_1, C_2 , and C_3 , corresponding to each of the three minima obtained from the various experiments, exhibited a degree of consistency which may be described by saying that the most extreme value, for any of these three points, has in no case differed from the mean of the values for that point by more than 0.2 per cent. It may be assumed that the error in the

determination of the area of the surface of adsorption does not exceed 0.2 per cent.

Since the determinations were made at constant temperature (22° C.) and with concentrations not greater than 1/750,000, or 0.000,001,333 gram per c.c. of water, it may be assumed safely that the error in the value of M used in the calculation is the same as the error in measuring the volume of the liquid used, which is not more than 0.1 per cent.

The possible error in M may be estimated, therefore, as follows:—

Factor.	Assumed error.
m	0.1 per cent.
C	0.2 „ „
A	0.2 „ „

and by reference to equation (1),

Factor.	Assumed error.
m^3	0.3 per cent.
$C_1 \cdot C_2 \cdot C_3$	0.6 „ „
A^3	0.6 „ „
	<hr/> 1.5 per cent.

This error of 1.5 per cent. can occur only if all the several errors—nine in number—happen to have their maximum value and are of the *same sign*, which is obviously highly improbable. A calculation of the probable error, on the assumption that each of the individual errors has its maximum value but that it may be + or — with equal probability, gives the value 0.13 per cent. To this value must be added, of course with due respect to sign, twice the value of any error in the value of δ . The various available values of δ are identical, and expressed as accurate to within 0.1 per cent. (Beilstein).

I believe, therefore, that the value of N calculated above is correct within 0.15 per cent., namely:

$$N = 6.003 \pm 0.08.$$

Discussion.

Although the practical results of this experimental work are quite satisfactory as far as accuracy to the 2nd decimal point is concerned, and in spite of the good accord of the

calculated value of N with the most reliable figures thus far published, it must be kept in mind that the assumptions on which this work is based are open to discussion, and that the writer's interpretation of the experiments may be incorrect. This may not forcibly affect the numerical results, but it may simply increase, by a small amount, the value of the error. One may conceive, indeed, that the real interpretation of the facts, although totally different from a theoretical thermodynamic point of view, might nevertheless yield quantitative results which would be infinitely close to those derived from an approximate interpretation. For instance, it is impossible to admit, theoretically, that all molecules are adsorbed. They certainly are not; but the percentage of non-adsorbed molecules is relatively so small that it only introduces into the calculation an error of the order of magnitude of the experimental errors. The remarkable concurrence of the figures on pp. 668-669 between the measured surface of adsorption and the product (area of adsorbed surface of each molecule \times number of molecules in solution) appears to furnish a striking proof of the adsorption of all molecules. However, the figures check only to the first decimal place, which in itself is very remarkable, but allows an error of ± 0.05 , or 0.20 per cent. As the area of the adsorbing surface can only be measured within approximately ± 0.2 per cent., there is room for a certain number of free molecules in the solution. The assumption that all molecules are adsorbed is undoubtedly incorrect, but probably correct to the second or third decimal place. Suppose that instead of having 26.6666×10^{-7} gram contained in one watch-glass, adsorbed on the surfaces, which is our assumption, we had only 26.6665×10^{-7} gram, and that 0.0001×10^{-7} was in the solution. This would mean almost 2×10^{10} free non-adsorbed molecules. But since it amounts to only a difference of about 0.0004 per cent. in the weight in grams, it does not affect our calculation, nor does it affect the determination of the molecular dimensions, which are submitted to much larger experimental errors.



SURFACE TENSION APPARATUS.—The tensiometer (du Noüy) is seen rolling on a rigid carriage provided with an efficient brake. The solutions are on the upper table, in watch-glasses, and can be raised very smoothly. It is fundamentally important that the solutions suffer no jarring or jerking during the two hours elapsing before the last measurements are taken, nor when raised to meet the platinum ring by means of which the measurements are performed.

LXVIII. *Regularities in Band Spectra.* By SNEHAMOY DATTA, D.Sc. (London), M.Sc. (Calcutta), Professor of Physics, Presidency College, Calcutta*.

[Plate XIV.]

1. *Introductory.*

THE analysis of band spectra into their component series has presented greater difficulty than the series classification of line spectra. In line spectra, the sorting out of the different series is facilitated by the experimental investigation of their Zeeman effect, pressure effect, and so forth, but such effects do not usually occur in band spectra. In the case of the less complicated band spectra, where there is an essential difference in the structure of the different groups, a classification can be made without any ambiguity; but in the absence of any such striking difference in the structure of the groups, it has been customary to select the series such that they conform with a particular type of formula. The formula which has been chiefly adopted for this purpose is one of the following type, originally proposed by Deslandres :

$$\nu = A + B[f(m)]^2 + C[f'(p)]^2,$$

where m and p take successive integral values, usually large and not within any definite limit, the form of the function of m and p being varied so as to make the best fit. Recently, however, Heurlinger† and Lenz‡, following the line of treatment suggested by Bjerrum§ and Schwarzschild||, have developed a theory which has been successful in explaining many of the characteristics of band spectra. The theory has been very little¶ applied to explain the characteristics of the series of heads appearing in a group of bands. In the present paper, starting with the equation suggested by these authors, an attempt has been made to arrive at a general equation which may explain the different types of series found to exist among the band heads.

* Communicated by the Author.

† Heurlinger, *Physik. Zeitschr.* xx. p. 188 (1919); *Zeitschr. f. Physik*, i. p. 82 (1920).

‡ Lenz, *Verhandl. d. Deutsch. Phys. Ges.* xxi. p. 632 (1919).

§ Bjerrum, *Nernst Festschrift*, p. 90 (1912).

|| Schwarzschild, *Berliner. Ber.* p. 548 (1916).

¶ Recently Kratzer (*Ann. der Physik*, lxxvii. p. 127, 1922), also Sommerfeld (English translation), p. 434, has developed a theory for the explanation of series in the CN bands. His line of treatment is, however, entirely different.

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2. *Theoretical.*

According to Heurlinger and Lenz, the bands are produced by a simultaneous quantum change of the rotation of the molecules ($M \rightarrow M'$), of the vibration of the atoms ($p \rightarrow p'$), and of the electron system of the molecule ($E \rightarrow E'$). The energy emitted by the molecule is the energy difference between the initial and final states in accordance with Bohr's frequency condition. These authors thus arrived at an equation of the type

$$\nu = \left[\frac{W_{E'} - W_E}{p} \right] + [(a'p' + b'p'^2) - (ap + bp^2)] + [A'M'^2 - AM^2], \quad \dots \quad (1)$$

where the first term within brackets represents the electron energy of the system, the middle one the energy of atomic vibration, and the last the energy of molecular rotation, in the final and initial conditions. The theory further maintains that the first two terms in equation (1) determine the characteristic frequency of a band (hence its position), whereas the quantum changes involved in the last term give its fine structure.

The system of discontinuous states corresponding to the quanta of atomic vibration is not stated, but it is possible to arrive at a physical interpretation in the following way. It is known from experiments which have nothing to do with spectra that a diatomic molecule can exist in at least two states which are discontinuously separated, namely the normal molecule and the normal atoms into which the molecule has dissociated. The other discontinuous states corresponding to the successive quantum changes must therefore be states of the molecule intermediate between these two states, or states of partial dissociation. And since for various reasons the atoms inside a molecule are regarded as linear oscillators—the vibration taking place along the line joining the nuclei—the partial dissociation will therefore be effected by the increase of the linear distance between the nuclei. Or in other words, the successive states correspond to the discontinuous increase in the linear distance between the nuclei. The atoms perform oscillations which are nearly but not quite harmonic, so that the energy in each state is given by

$$W_p = h(ap + bp^2),$$

where p refers to the numerical order of the successive states. With the change in the linear distance between the nuclei,

there will be a change in the position of the electron which serves as the connecting link between the atoms. Consequently, corresponding to each orbit* of the atom it would be natural to expect one orbit of the link electron, the change from one orbit to another causing the radiation of the electron energy. But the approximate constancy of the first term in equation (1) seems to suggest that the electron has only two definite discontinuous states, possibly the bound and the free states, corresponding to the partially and completely dissociated states of the molecule.

The question of electron energy is, however, very obscure, and as it does not come within the scope of the present paper, it will not be further considered. In any case, the maximum of energy that can be radiated would correspond to a return of the atom from the limiting to its primary orbit.

Besides these two changes, there is another—viz., the energy of rotation of the molecule as a whole—which has to be taken into consideration. But the change of rotational energy involves only a very small change in the electron energy and in the vibrational energy† of the atoms which give rise to the head‡ of a band. As the present paper deals with the regularities present among the band heads, the last term in equation (1) corresponding to the rotational

* The orbits here referred to are the limited number of possible dissociated states of the molecule. The term has been used to maintain the analogy with the stationary electron orbits of Bohr.

† Kratzer has worked out this mutual action, and has represented it by $-m^2 a_n h$, where m is the rotational quantum and a_n is proportional to the oscillation quantum n (see 'Atomic Structure and Spectral Lines,' by Sommerfeld (English translation), p. 422). The shift due to the mutual action is therefore very small, and as the numerical relations in the band heads mainly involve the differences in wave-numbers between the bands having the same rotational quantum, the shift may be neglected altogether.

‡ More correctly speaking, the characteristic frequency ν_0 , which determines the position of the band. According to the theory of band spectra, the head of a band, as has been clearly pointed out by Curtis (Proc. Roy. Soc. A, ci. pp. 38-64), assumes only a secondary importance, it being a region where the lines happen to crowd together. The relation established in the present paper is therefore one to be expected among the characteristic frequencies ν_0 of each band. But owing to our want of knowledge of the structure of each band, it is not possible at present to seek for numerical relations amongst the characteristic frequencies of the bands. Curtis, however, has pointed out the definiteness of the relation between the apparent head of a band and its characteristic frequency [$\nu = \nu_0 + h/8\pi^2(I - I')$]. As I , I' remain constant for the same system of bands, the numerical relations, which involve mainly the differences in wave-numbers, will be the same whether the frequency of the apparent head (ν) or the characteristic frequency (ν_0) are taken into consideration.

energy can be left out, so that equation (1) is modified to

$$\nu = \frac{W_{E'} - W_E}{h} + [(a'p' + b'p'^2) - (ap + bp^2)], \quad (2)$$

where p' and p refer to the initial and final orbits of the vibrating atoms. Had the oscillation been a purely harmonic one, the principle of correspondence would have required that p should never change by more than one unit. Consequently, though the oscillation is not strictly harmonic, but very nearly so, it is reasonable to suppose that the more probable changes are those that involve a change of one unit—*i. e.*, the radiation takes place in a change from the $p+1$ to the p orbit. Now in the ordinary condition the molecules are in different partially dissociated states—*i. e.*, the atoms are in different orbits, the most probable orbit being a function of temperature. The final orbit p is therefore not the same for all molecules, but is of the form $p = k + m$, where k determines the minimum order number of the atom (*i. e.*, corresponding to the shortest distance between the nuclei) and m takes all the ordinal values including zero. The general equation for such radiation will then be of the form

$$\begin{aligned} \nu &= \frac{W_{E'} - W_E}{h} + [\{a'(k+m+1) + b'(k+m+1)^2\} \\ &\quad - \{a(k+m) + b(k+m)^2\}] \\ &= \frac{W_{E'} - W_E}{h} + a' + b' + 2k \cdot b' + k(a' - a) + k^2(b' - b) \\ &\quad + m[(a' - a) + 2b' + 2k(b' - b)] + m^2(b' - b) \\ &= A + Bm + Cm^2, \quad \dots \dots \dots (3) \end{aligned}$$

where

$$B = (a' - a) + 2b' + 2k(b' - b) \quad \text{and} \quad C = (b' - b).$$

As b' is a small number and all other terms are differences of numbers of the same order of magnitude, B cannot be large and C must be exceedingly small. The characteristic of such a group of heads would be a close succession of heads with the intervals very slowly varying.

This class of bands is the most general one, and has been recognized before, this type of equation being previously used empirically to arrange into series various groups of bands*.

* The bands of alkaline earth fluorides have all been arranged into this form (see Proc. Roy. Soc. A, xcix. p. -).

In some cases, however, it may happen that the molecules are not in different dissociated states, but are all in one state, the primary state corresponding to k in equation (3). In this case the final orbit is the same for all molecules—namely k , and radiation takes place by a change from any unstable orbit to which the atoms are brought under stimulus to the same primary orbit k . Evidently, as the quantum change involved is more than unity, the excitation of such radiations would require a more powerful discharge than that necessary for the previous case. The hypothesis of one primary state means that such molecules are in a more stable state, so that partial dissociation caused by collision with neighbouring molecules or otherwise is not taking place. The equation for such radiation would be of the form

$$\begin{aligned} \nu &= \frac{W_{E'} - W_E}{h} + [\{a'(k+n) + b'(k+n)^2\} - \{a(k) + bk^2\}] \\ &= \frac{W_{E'} - W_E}{h} + k(a' - a) + k^2(b' - b) + n(a' + 2b'k) + n^2b' \\ &= A + Bn + Cn^2, \end{aligned} \quad (4)$$

where

$$B = a' + 2b'k \quad \text{and} \quad C = b'.$$

The form of the equation is the same, but the constants B and C have values of different magnitude. The numerical calculations of the constants are not yet possible, but clearly, as they do not involve any differences as in equation (3), their values are greater. As b' is a small number (being the coefficient of the second term in the Fourier series), the value of B is of the same order of magnitude as a' —the natural frequency of vibration of the atom. Information based on the specific heat of a diatomic gas gives a' of the order 1000 in wave-number. Hence B is > 1000 . The constant C is the same as b' , and is therefore a small number but greater than its value in equation (3), where it is expressed as a difference ($b' - b$). The character of such a group of heads would therefore be a succession of heads with long intervals (of order greater than 1000), the successive intervals varying faster in this than in the previous case.

The third and the fourth positive bands of nitrogen may well answer to this class, both numerically and in their methods of excitation.

In the most general cases all the possible primary states and all the possible quantum changes are to be expected. This is the case most analogous to the radiation of line

spectra, so that there is a change from any orbit to any other orbit. The equations (3) and (4) could then be combined as

$$\begin{aligned}
 \nu &= \frac{W_{E'} - W_E}{h} [\{a'(k+m+n) + b'(k+m+n)^2\} \\
 &\quad - \{a(k+m) + b(k+m)^2\}] \\
 &= \frac{W_{E'} - W_E}{h} + k(a' - a) + k^2(b' - b) + m[(a' - a) + 2b'n \\
 &\quad + 2k(b' - b)] + m^2(b' - b) + n(a' + 2b'k) + b'n^2 \\
 &= A + m[D + 2b'n] + m^2C' + nB' + b'n^2, \quad . \quad . \quad . \quad (5) \\
 &= A + mD + m^2C' + n(B' + 2b'm) + b'n^2, \quad . \quad . \quad . \quad (5a)
 \end{aligned}$$

where

$$A = \frac{W_{E'} - W_E}{h} + k(a' - a) + k^2(b' - b),$$

$$D = (a' - a) + 2k(b' - b),$$

$$C' = (b' - b),$$

$$B' = a' + 2b'k.$$

The order of magnitude of B' will be that of B in (4)—*i. e.*, > 1000 — C' is a very small quantity and is of the order of C in (3), D is also of the same order as B in (3), and determines the change in the natural frequency of the atom due to the change of state. The characteristic of such heads will therefore be a succession of several groups of heads, the groups following at long intervals (order > 1000), but the heads in each group—*i. e.*, the subheads—following at short intervals.

The equations (5) and (5a) are therefore the general equations which should represent the regularities in the band heads. They essentially differ from Deslandres' empirical formula in the numerical values of n and m , which are here simple integers, having definite physical meaning (m refers to the primary orbit of the atom, and n to change of quantum) unlike the arbitrary high integers used by Deslandres.

In the following sections a typical system of bands has been studied with a view to examining the applicability of the above equation.

Regularities in the First Positive Bands of Nitrogen.

The nitrogen bands of wave-lengths longer than λ 5000, known as the first positive bands, consist of a number

(about 50) of similar sub-groups of bands. With moderate dispersion each sub-group is seen to be composed of several (usually five) bands degrading towards the violet. Regularities of separation appear amongst the corresponding heads of the successive 8 to 10 sub-groups. The interval then changes abruptly, and continues to be regular for the next 8 or 10 groups, and so on. Accordingly, the 8 or more of these sub-groups, capable of representation in series of the ordinary type, have been designated as a group. The entire set of first positive bands is thus composed of 5 and possibly 6 such groups, which are designated *a* to *f* respectively. The nomenclature has been adopted after Von der Helm *, who suggested this to be the best method of grouping the bands (see III., Pl. XIV.).

A second arrangement of the bands was first suggested by Cuthbertson † and subsequently improved by Deslandres ‡ (see II., Pl. XIV.). In this arrangement the head of a band in one of the above sub-groups is related not to the corresponding head in the adjacent sub-groups, but to that of a sub-group in the adjacent group. The entire set has thus been represented by the formula

$$\nu = 22785 \cdot 1 - \frac{30 \cdot 319}{8} (2m)^2 + \frac{29 \cdot 363}{8} (2p + 1)^2,$$

where *m* varies from 44 to 53, and *p* from 43 to 48.

In the present section, criticisms of the two existing arrangements have been attempted and a third arrangement proposed (see I., Pl. XIV.). This new arrangement, besides removing the existing defects, shows remarkable agreement with the theoretical formula previously discussed.

The defect of the Von der Helm arrangement lies in the grouping of the sub-groups. On the ground of numerical relations, it is essentially necessary that the spacing of the heads should be the same for all the sub-groups belonging to the same group. Out of this consideration, the data collected from the very exhaustive paper on the subject by Birge § clearly lead to the conclusion that the grouping ought to be different in some respects from that adopted by Von der Helm.

The data for the consideration of the grouping are given

* Von der Helm, *Zeit. f. Wiss. Phot.* viii. p. 405 (1910).

† Cuthbertson, *Phil. Mag.* (6) iii. p. 348 (1902).

‡ Deslandres, *Comptes Rendus*, cxxxiv. p. 747 (1902).

§ Birge, *Astrophys. Journ.* xxxix. pp. 50-88 (1914).

in Table I. The first two columns show the previous denomination used by Birge after Von der Helm, and the one adopted in the present paper. The third and the fourth

TABLE I.

Sub-groups.					
Birge after Von der Helm.	Datta.	λ . I. A.	ν .	Difference.	Remarks.
I d_4	I c_2	6788·614	14730·53		
IV d_4	IV c_2	758·054	797·12	66·59	
I d_5	I c_3	6704·755	14914·79		
IV d_5	IV c_3	674·908	981·48	66·69	
I d_6	I c_4	6623·574	15097·59		
IV d_6	IV c_4	594·418	164·34	66·75	
I d_7	I c_5	6544·881	15279·13		
IV d_7	IV c_5	16·403	345·90	66·77	
I d_8	I c_6	6468·597	15459·31		
IV d_8	IV c_6	40·768	526·10	66·79	
I d_9	I c_7	6394·628	15638·12		
IV d_9	IV c_7	67·416	704·96	66·84	
I d_{10}	I c_8	6322·816	15815·74		
IV d_{10}	IV c_8	296·212	882·57	66·83	
I d_{11}	I c_9	6252·806	15992·81		
IV d_{11}	IV c_9	26·978	6059·15	66·35	
I d_{12}	I c_{10}	6185·127	16167·82		
IV d_{12}	IV c_{10}	59·692	234·57	66·75	
<hr/>					
	I d_0	Not recorded.
I e_1	I d_1	6186·733	16163·62		
IV e_1	IV d_1	61·648	229·42	65·80	
I e_2	I d_2	6127·374	16320·20		
IV e_2	IV d_2	02·736	386·09	65·89	
I e_3	I d_3	6069·663	16475·38		
IV e_3	IV d_3	45·484	541·27	65·89	
I e_4	I d_4	6013·575	16629·04		
IV e_4	IV d_4	5989·812	694·73	65·69	
I e_5	I d_5	5959·053	16781·19		
IV e_5	IV d_5	35·740	847·10	65·91	
I e_6	I d_6	5906·010	16931·90		
IV e_6	IV d_6	883·146	997·70	65·80	
I e_7	I d_7	5854·404	17081·16		
IV e_7	IV d_7	32·054	146·62	65·46	
I e_8	I d_8	5804·135	17229·10		
IV e_8	IV d_8	782·059	294·87	65·77	
I e_9	I d_9	5755·188	17375·62		
IV e_9	IV d_9	35·555	441·19	65·57	
I e_{10}	I d'_{11}	5707·580	17520·56		
IV e_{10}	IV d'_{11}	685·199	589·53	68·97	
I e_{11}	I d'_{12}	5660·842	17665·22		
IV e_{11}	IV d'_{12}	38·868	734·06	68·84	
I e_{12}	I d'_{13}	5615·318	17808·43		
IV e_{12}	IV d'_{13}	No data.

Sub-groups.

Table I. (continued).

Birge.	Data.	λ . I.A.	ν .	Difference.	Remarks.
I e_{13}	I d'_{14}	5570·777	17950·82	24·31	* 24·43
II e_{13}	II d'_{14}	63·244	975·13		
I e_{14}	I d'_{15}	5527·150	18092·55		
II e_{14}	II d'_{15}	19·682	116·98		
I e_{15}	I d'_{16}	5584·338	18233·75		No data.
II e_{15}	II d'_{16}	
	I e_0	Not recorded.
I f_1	I e_1	5632·75	17753·32		No data.
IV f_1	IV e_1	
I f_2	I e_2	5592·881	17879·87	65·89	65·83
IV f_2	IV e_2	72·347	945·76		
I f_3	I e_3	5553·730	18005·91	65·83	65·41
IV f_3	IV e_3	33·504	071·74		
I f_4	I e_4	5515·594	18130·40	65·41	65·50
IV f_4	IV e_4	95·763	95·81		
I f_5	I e_5	5478·471	18253·27	65·50	65·45
IV f_5	IV e_5	58·879	318·77		
I f_6	I e_6	5442·325	18374·50	65·45	65·36
IV f_6	IV e_6	23·014	439·95		
I f_7	I e_7	5407·129	18494·10	65·36	65·44
IV f_7	IV e_7	388·087	559·46		
I f_8	I e_8	5372·820	18612·20	65·44	57·87
IV f_8	IV e_8	53·992	677·64		
I f_9	I e'_{11}	5339·432	18728·59	57·87	No data.
IV f_9	IV e'_{11}	22·983	86·46		
I f_{10}	I e'_{12}	5306·859	18843·53		No data.
IV f_{10}	
I f_{11}	I e'_{13}	5275·072	18957·10		No data.
IV f_{11}	IV e'_{13}	
I f_{12}	I e'_{14}	5244·071	19069·16		No data.
IV f_{12}	IV e'_{14}	
I f_{13}	I e'_{15}	5213·808	19179·84	64·36	64·13
IV f_{13}	IV e'_{15}	196·370	244·20		
I f_{14}	I e'_{16}	5184·237	19289·24	64·13	No data.
IV f_{14}	IV e'_{16}	67·060	353·37		
I f_{15}	I e'_{17}	5155·323	19397·42		No data.
IV f_{15}	
I f_{16}	I e'_{18}	5126·806	19505·11		No data.
IV f_{16}	

* The fourth band is not recorded; but the difference between the first and second band in each sub-group shows that they belong to the same series.

columns give the wave-lengths and wave-numbers of the first and fourth band in each sub-group, the second, third, and the fifth being omitted for the sake of brevity. The fifth column gives the difference in wave-numbers of the two bands. When the head has not been definitely marked out by Birge, the strongest line on the red side has been taken as the head.

The fifth column of Table I., which gives the interval between the heads, clearly indicates that, using the old nomenclature, all the sub-groups from d_4 to d_{12} belong to the same series. The name of the series has been changed from d to c , because according to the new classification all the sub-groups on the less refrangible side are clustered into two groups (a, b), and not into three groups (a, b, c) as previously suggested by Von der Helm.

The numbering of each sub-group has to be changed also, but the previous idea of counting the sub-groups from the long wave-length side has been adopted.

Referring back to column 5 (Table I.) and using the old nomenclature, the spacing of the heads appears to remain nearly constant up to e_9 , after which it suddenly changes, but remains constant for the next two members. From e_{12} to e_{15} the data are insufficient to show whether these latter members belong to the same series as e_{10} and e_{11} . In any case, the regular series consists of the sub-groups e_1 to e_9 , and they have been re-named as d_0 to d_8 in accordance with the nomenclature adopted for the preceding series. For reasons which will be mentioned later, the remaining sub-groups are regarded as belonging to a different system (d') having no apparent relation with the one which forms the regular series. Following the same analysis, the sub-groups f_1 to f_8 are regarded as the regular series, whereas the later members from f_9 to f_{15} are excluded; they perhaps belong to the previous irregular system.

Fresh support in favour of the revision of groupings as suggested in this paper has been obtained from an examination of the intensity of the sub-groups. In both the old e and f groups, the intensity of the sub-groups suddenly diminishes after e_9 and f_8 —that is, exactly where the divisions have been made. The old f group presents two distinct maxima—one at f'_5 and the other at f_{12} . In the e group also, besides the first maximum at e_6 there is an indication* of a second maximum at e_{13} .

The presence of two maxima in the same series is contrary to our existing knowledge of band spectra. According to the grouping adopted here, there is only one sub-group showing the maximum of intensity, and this is roughly in the middle of each group.

Further evidence in justification of the above mode of division is obtained by examining the structure of the bands constituting each sub-group. In the first heads of

* This is not very pronounced owing to the overlapping of some of the f sub-groups.

the members of the f group there appears an extremely heavy doublet. Birge, from consideration of (1) the spacing of this doublet and (2) the numerical relation of the series, has suggested that "the group consists really of two groups." Although Birge did not record any such doublet in the first heads of the members of the e group, the existence of a second line on the more refrangible side of the first head has been traced in all the sub-groups. The differences in wave-numbers of these two lines for the entire sub-groups of the old e group are :—

	$e_{1\cdot}$	$e_{2\cdot}$	$e_{3\cdot}$	$e_{4\cdot}$	$e_{5\cdot}$	$e_{6\cdot}$	$e_{7\cdot}$	$e_{8\cdot}$
Diff. in wave-numbers ...	1·14	1·15	1·04	1·05	1·12	1·0	1·08	1·06

	$e_{9\cdot}$	$e_{10\cdot}$	$e_{11\cdot}$	$e_{12\cdot}$	$e_{13\cdot}$	$e_{14\cdot}$	$e_{15\cdot}$
Diff. in wave-numbers ...	1·0	0·36	0·41	0·42	0·50	0·41	0·38

The spacing of the two lines thus continues to be very nearly constant up to e_9 ; it then changes, and again remains roughly constant up to the end of the group, suggesting that the e group likewise consists of two groups.

Thus from various considerations of numerical relationships and otherwise, the mode of grouping suggested in this paper seems to be most significant. And this form of arrangement being essentially similar to that of Von der Helm, has all the advantages over the Cuthbertson arrangement already pointed out by Birge, viz.:—"It is possible to fit a greater number of lines into the simple series of the Von der Helm arrangement of bands than into the more complex two-parameter formula indicated by the Cuthbertson arrangement."

In the second form of arrangement proposed by Cuthbertson a band in one of the sub-groups is related, not to the corresponding band in the adjacent sub-group, but to that of a sub-group in the adjacent group. Thus, according to his arrangement, there are as many vertical series as the maximum number of sub-groups in a group, so that the vertical series are the same as adapted here. The horizontal series, however, instead of representing the relation between all the sub-groups in a group (as the present arrangement does), are picked out in the way which best fits in with the empirical formula quoted before. The horizontal series in his arrangement consists of members which fall on lines parallel to the diagonal drawn in Table II.

It is a very important condition for the fulfilment of series-relations that the spacing of the bands must be the same for the sub-groups constituting one series. The spacing

of the bands has been calculated in Table I. (column 5) for the four groups, *c*, *d*, *e*, and *f*. It is therefore clear that in Cuthbertson's arrangement, neither the sub-groups forming the horizontal series nor those forming the vertical series have the same spacing. In the present arrangement the sub-groups in a horizontal series have very nearly the same spacing, but those in a vertical series have slightly different spacing, the difference being an actual one, and not due to any error of measurement. An explanation is given in the following way. Why each sub-group has so many bands (under small dispersion three) is not completely understood. In connexion with the iodine fluorescent bands, it has been suggested * that some change in rotational energy causes the displacement of the band heads. The same thing might be happening with nitrogen. The change in rotational energy may be caused by a change in the moment of inertia of the molecule. The moment of inertia of a diatomic molecule can be calculated by assuming the masses m_1 and m_2 of the atoms concentrated at the nuclei. If they are at a distance l apart, then

$$I = \frac{m_1 m_2}{m_1 + m_2} l^2.$$

According to what has been put forward in the theoretical section, the different orbits of the atoms correspond to different distances between the nuclei; consequently, I should be different for different orbits. A change in I corresponds to a change in l , and is therefore likely to be very nearly the same for the same quantum change but different for different quantum changes. Now, the bands in the horizontal series, according to the present scheme, refer to the same quantum change, whereas those in vertical series correspond to different quantum changes; consequently, the same spacing in the horizontal series and different spacing in the vertical series are what we should expect.

On the other hand, a change in physical condition of the source has been suggested as an indication that the Cuthbertson arrangement may be more significant. Fowler and Strutt † have shown that the spectrum of the active modification of nitrogen shows certain of the sub-groups of the 1st positive bands greatly intensified, while the others are very faint. Those intensified formed three successive horizontal rows according to Cuthbertson's arrangement, whereas they had no apparent significance according to that of Von der Helm. But according to the present arrangement they

* W. Lenz, *Phys. Zeit.* xxi. p. 691 (1920); Kratzer, *Zeit. für Physik*, (3), v. p. 289 (1920).

† Fowler & Strutt, *Proc. Roy. Soc.* lxxxv. p. 377 (1911).

are the last three members in the horizontal series. So that it may be inferred that the nature of the stimulus in the afterglow is such as to develop the higher members of a series. The enormous concentration of energy at the end of the afterglow CN bands also supports this view. In a separate section the nature of the afterglow spectrum will be discussed in the light of the present theory.

Another change in physical condition is to be noticed in the experiments of Angerer*, who made a comparative study of these bands at the ordinary temperature and that of liquid air. The main results of his experiments are that at low temperature all the sub-groups are weak, sometimes only the first band in each sub-group appearing; but some of the sub-groups comparatively retain their intensity, and thereby appear to be stronger than the others. Generally speaking, these are either the stronger members of the sub-groups appearing under the ordinary condition of discharge, or the earlier numbers of these sub-groups which have been left out of the regular groups, *d*, *e*, etc., and have been recognized as forming altogether different groups, named as the *d'* and *e'* groups. As belonging to the first class may be mentioned the bands at $\lambda 6623.5$ (new *c*₃), $\lambda 6069.6$ (new *d*₂) and $\lambda 5478.4$, $\lambda 5442.3$, $\lambda 5407.1$, $\lambda 5372.8$ (new *e*₄, *e*₅, *e*₆, and *e*₇). Whereas the bands at $\lambda 5615.3$, $\lambda 5570.7$ (new *d'*₃ and *d'*₁), $\lambda 5339$, $\lambda 5306$ (new *e'*₁ and *e'*₂) belong to the second class. These latter bands are also those which are very weak at ordinary temperature. Roughly speaking, therefore, the groups whose regularities have been definitely established consist of sub-groups which are stronger under the ordinary condition of the discharge-tube but weaker at low temperatures; whereas those groups (named with dashes) whose regularities are not so definitely shown on account of the insufficiency of their number, consist of sub-groups which are weak under ordinary circumstances and comparatively strong at low temperature. The behaviour at low temperature is hardly explicable by either of the Von der Helm or Cuthbertson arrangements, but the present arrangement explains it in a very significant way.

Eliminating † in this way a few of the sub-groups, for the various reasons pointed out above, those remaining have been

* Angerer, *Ann. der Phys.* xxxii. p. 549 (1910).

† It must be made sufficiently clear that even if these sub-groups be included in the corresponding group, the scheme of arrangement suggested in the paper stands. Only the *m*—the quantum number of the successive orbits—has to be increased (see Table II.) This would then indicate that at ordinary temperature the stimulus creates some more unstable orbits than are expressed in Table II., but at lower temperatures the higher members are suppressed.

arranged as shown in Table II. The successive integral values of m on a horizontal line refer to the successive orbits of the atoms in falling back to where the radiation is supposed to occur; the corresponding values of n , written in brackets, determine the change of number of orbits (quantum changes) involved in the fall. Thus the first number in group a is due to a fall from the 1st quantum orbit to the 0th one, the second to a fall from the 2nd orbit to the 1st, and so on. Similarly, in group f , the first is due to a fall from the 2nd quantum orbit to the 0th one, the second for a fall from the 3rd orbit to the 1st, and so on.

In Table II. the observed wave-lengths and the calculated wave-numbers of the first heads of each sub-group are collected, and the difference in wave-numbers between the successive sub-groups are shown at the top. Each horizontal row thus represents a series of the usual type, expressible by an equation:

$$\nu = A + Bm + c'm^2.$$

Proceeding from one series to another, the differences between the corresponding adjacent sub-groups—roughly expressed by the constant B —gradually decrease by a constant amount. Taking the $m=0$ th member of each series as its head, the relation between the different heads may be conveniently expressed as shown in Table III.

TABLE III.

Series n .	ν .	$\delta\nu$.	$d(\delta\nu)=2b'$.	$\Delta\nu=B$.	$d(\Delta\nu)$.
0	9244.8	1733.7			
1	10978.5	1704.7	29.0	245.0	
2	12688.2	1675.7	29.0	216.0	29.0
3	14358.9	1646.7	29.0	187.0	29.0
4	16005.6	1617.7	29.0	158.0	29.0
5	17623.3	1588.7	29.0	129.0	29.0
6	19212.0			100.0	

The vertical series, given in the second column of the above table, is also of the ordinary type expressible in the form:

$$\nu = A + B'n + b'n^2.$$

TABLE II.—Showing the Arrangement of the First Head of First Positive Bands of Nitrogen.

<i>m</i> .	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	Remarks.
Groups. <i>n</i> .														
[0]	$\begin{cases} 1.06 \mu \\ 9244.8 \\ 189 \end{cases}$	—												Measures from Coblentz, probable error 0.1 μ .
<i>a</i> . [1]	$\begin{cases} 9101 \\ 10978.5 \\ 9.2 \end{cases}$	$\begin{cases} 245.0 \\ 11223.5 \\ 8.7 \end{cases}$	$\begin{cases} 8903 \\ 243.6 \\ 11467.1 \\ 17.9 \end{cases}$	$\begin{cases} 8707 \\ 242.2 \\ 11709.3 \\ -1.1 \end{cases}$	$\begin{cases} 8541 \\ 240.8 \\ 11950.1 \\ -1.2 \end{cases}$	$\begin{cases} 8369 \\ 239.4 \\ 12189.5 \\ -0.3 \end{cases}$	$\begin{cases} 8204 \\ 238.0 \\ 12427.5 \\ 5.7 \end{cases}$	$\begin{cases} 8043 \\ 236.6 \\ 12664.1 \\ — \end{cases}$	$\begin{cases} 235.2 \\ 12899.3 \\ — \end{cases}$	$\begin{cases} 233.8 \\ 13133.1 \\ — \end{cases}$	$\begin{cases} 232.4 \\ 13365.5 \\ — \end{cases}$	$\begin{cases} 231.0 \\ 13396.5 \\ — \end{cases}$	$\begin{cases} 229.6 \\ 13428.1 \\ — \end{cases}$	Measures from Croze, probable error "several angstroms."
<i>b</i> . [2]	$\begin{cases} 7887 \\ 12683.2 \\ -4.1 \end{cases}$	$\begin{cases} 216.1 \\ 12899.2 \\ 17.3 \end{cases}$	$\begin{cases} 7742 \\ 214.6 \\ 13113.8 \\ 1.3 \end{cases}$	$\begin{cases} 7624.8 \\ 213.1 \\ 13326.9 \\ -3.5 \end{cases}$	$\begin{cases} 7505.6 \\ 211.6 \\ 13538.5 \\ 0.4 \end{cases}$	$\begin{cases} 7386.1 \\ 210.1 \\ 13748.6 \\ -1.0 \end{cases}$	$\begin{cases} 7274.0 \\ 208.6 \\ 13957.2 \\ -0.5 \end{cases}$	$\begin{cases} 7165.0 \\ 207.1 \\ 14164.3 \\ 0.8 \end{cases}$	$\begin{cases} 7059.6 \\ 205.6 \\ 14369.9 \\ — \end{cases}$	$\begin{cases} 6954.1 \\ 204.1 \\ 14574.0 \\ — \end{cases}$	$\begin{cases} 6848.6 \\ 202.6 \\ 14776.6 \\ — \end{cases}$	$\begin{cases} 6743.1 \\ 201.5 \\ 14978.1 \\ — \end{cases}$	$\begin{cases} 6637.6 \\ 200.0 \\ 15180.6 \\ — \end{cases}$	Measures from Birge taken on the Hilger spectroscope, probable error 1 Å.
<i>c</i> . [3]	$\begin{cases} 6986.0 \\ 14358.9 \\ -7.6 \end{cases}$	$\begin{cases} 187.0 \\ 14545.9 \\ -1.5 \end{cases}$	$\begin{cases} 6875.5 \\ 185.58 \\ 14731.48 \\ -0.92 \end{cases}$	$\begin{cases} 6788.61 \\ 184.18 \\ 14915.65 \\ -0.86 \end{cases}$	$\begin{cases} 6704.75 \\ 182.78 \\ 15098.44 \\ -0.84 \end{cases}$	$\begin{cases} 6623.57 \\ 181.38 \\ 15279.82 \\ -0.69 \end{cases}$	$\begin{cases} 6544.88 \\ 179.98 \\ 15459.80 \\ -0.50 \end{cases}$	$\begin{cases} 6468.60 \\ 178.58 \\ 15638.38 \\ -0.26 \end{cases}$	$\begin{cases} 6394.63 \\ 177.18 \\ 15815.56 \\ 0.17 \end{cases}$	$\begin{cases} 6322.82 \\ 175.78 \\ 15991.34 \\ 1.47 \end{cases}$	$\begin{cases} 6252.81 \\ 174.38 \\ 16165.72 \\ 2.09 \end{cases}$	$\begin{cases} 6185.13 \\ 172.98 \\ 16340.15 \\ 2.69 \end{cases}$	$\begin{cases} 6117.45 \\ 171.58 \\ 16514.56 \\ 3.29 \end{cases}$	Measures from Birge, probable error 0.02 Å.
<i>d</i> . [4]	$\begin{cases} — \\ 16905.6 \\ — \end{cases}$	$\begin{cases} 158.0 \\ 16163.62 \\ 0.01 \end{cases}$	$\begin{cases} 6180.73 \\ 156.58 \\ 16320.20 \\ 0.01 \end{cases}$	$\begin{cases} 6127.37 \\ 155.13 \\ 16475.33 \\ 0.06 \end{cases}$	$\begin{cases} 6069.66 \\ 153.68 \\ 16629.01 \\ 0.02 \end{cases}$	$\begin{cases} 6013.58 \\ 152.23 \\ 16781.24 \\ -0.04 \end{cases}$	$\begin{cases} 5959.05 \\ 150.78 \\ 16932.02 \\ -0.12 \end{cases}$	$\begin{cases} 5906.01 \\ 149.33 \\ 17081.35 \\ -0.18 \end{cases}$	$\begin{cases} 5854.40 \\ 147.88 \\ 17229.23 \\ -0.15 \end{cases}$	$\begin{cases} 5804.14 \\ 146.43 \\ 17375.66 \\ -0.04 \end{cases}$	$\begin{cases} 5755.19 \\ 144.98 \\ 17520.00 \\ — \end{cases}$	$\begin{cases} 5706.24 \\ 143.53 \\ 17665.34 \\ — \end{cases}$	$\begin{cases} 5657.29 \\ 142.08 \\ 17810.62 \\ — \end{cases}$	No.
<i>e</i> . [5]	$\begin{cases} — \\ 17623.3 \\ — \end{cases}$	$\begin{cases} 129.1 \\ 17752.32 \\ 1.00 \end{cases}$	$\begin{cases} 5632.75 \\ 127.58 \\ 17879.90 \\ -0.03 \end{cases}$	$\begin{cases} 5592.88 \\ 126.03 \\ 18005.98 \\ -0.07 \end{cases}$	$\begin{cases} 5553.73 \\ 124.58 \\ 18130.56 \\ -0.14 \end{cases}$	$\begin{cases} 5515.59 \\ 123.08 \\ 18253.64 \\ -0.37 \end{cases}$	$\begin{cases} 5478.47 \\ 121.58 \\ 18375.22 \\ -0.74 \end{cases}$	$\begin{cases} 5442.33 \\ 120.08 \\ 18495.30 \\ -1.68 \end{cases}$	$\begin{cases} 5407.13 \\ 118.58 \\ 18613.88 \\ -1.20 \end{cases}$	$\begin{cases} 5372.82 \\ 117.08 \\ 18737.96 \\ — \end{cases}$	$\begin{cases} 5338.51 \\ 115.58 \\ 18862.04 \\ — \end{cases}$	$\begin{cases} 5304.20 \\ 114.08 \\ 18986.12 \\ — \end{cases}$	$\begin{cases} 5269.89 \\ 112.58 \\ 19110.20 \\ — \end{cases}$	No.
<i>f</i> . [6]	$\begin{cases} — \\ 19212.0 \\ — \end{cases}$	$\begin{cases} 100.1 \\ 19312.0 \\ — \end{cases}$	$\begin{cases} 98.6 \\ 19410.6 \\ -7.1 \end{cases}$	$\begin{cases} 97.1 \\ 19507.7 \\ -1.2 \end{cases}$	$\begin{cases} 95.6 \\ 19603.3 \\ 9.5 \end{cases}$	$\begin{cases} 94.1 \\ 19697.4 \\ — \end{cases}$	$\begin{cases} 92.6 \\ 19790.0 \\ -2.1 \end{cases}$	$\begin{cases} 91.1 \\ 19881.1 \\ -3.5 \end{cases}$	$\begin{cases} 89.6 \\ 19972.2 \\ — \end{cases}$	$\begin{cases} 88.1 \\ 20063.3 \\ — \end{cases}$	$\begin{cases} 86.6 \\ 20154.4 \\ — \end{cases}$	$\begin{cases} 85.1 \\ 20245.5 \\ — \end{cases}$	$\begin{cases} 83.6 \\ 20336.6 \\ — \end{cases}$	* Measures from Angstrom & Thalen. * Visually observed by Fowler & Strutt.

1st line gives the observed wave-lengths.
 2nd line gives the successive differences in the calculated wave-numbers.
 3rd line gives the calculated wave-numbers.
 4th line gives the difference between the observed and the calculated wave-numbers ($r_0 - r_c$).

Combining the two, the general equation is of the form :

$$\nu = A + Bm + c'm^2 + B'n + b'n^2,$$

n remaining constant, variations of m give the horizontal series, and m remaining constant, variation of n gives the vertical series. The coefficient B changes from one horizontal series to another by a constant multiple, as shown in columns 5 and 6 of the preceding table. B is therefore of the form $B = D + 2b'n$, where D is a constant. The general equation is thus reduced to

$$\nu = A + m(D + 2b'n) + c'm^2 + B'n + b'n^2,$$

a form identical with the theoretically deduced equation (5). An approximate solution of the general equation can be given by

$$\begin{aligned} \nu = 9244.8 + m(274.75 - 29.0n) + (-0.75)m^2 \\ + 1748.2n + (-14.5)n^2. \end{aligned}$$

The values of the various constants are of the same order as predicted by the theoretical equation.

In the arrangement shown in Table II. it has been assumed that the stimulus creates comparatively unstable orbits up to 13, and that radiation takes place in the fall from these unstable orbits to those of comparatively greater stability by change of 1, 2, or more quanta. Thus, as one proceeds downwards, the groups corresponding to higher quantum changes must have one sub-group less than the previous one. Thus the group e , with a quantum change of 5, cannot have any sub-group beyond the one corresponding to the 8th orbit, and so on. At the same time the group with zero quantum change cannot have more than one sub-group; for the absence of a quantum change means the absence of the atomic vibration; consequently the only radiation possible is that due to a change of the electron energy. As this may involve a change of the rotational energy of the molecule as a whole, the total radiation would correspond to that of only one sub-group with its first head at 1.08μ , as calculated by an interpolation of the data shown in column 2 of Table II. Arranging the sub-groups empirically, a glance at Table II. would indicate that there should be a succession of sub-groups in the first horizontal row instead of the single one as predicted by the theory. Coblentz *, from the infra-red measurements of the emission

* W. W. Coblentz, Publication No. 35, Carnegie Institution of Washington.

spectra of vacuum tubes, has recorded a sharp maximum at 1.06μ . The sharpness of the maximum would indicate the presence of a single band, thus proving the validity of the above suggestion.

With regard to the other groups having quantum changes 1, 2, etc., Table II. shows that all the calculated members have not been actually observed. Peculiarly, however, with small quantum changes the bands corresponding to the higher orbits are missing, and with higher quantum changes those corresponding to the lower orbits are missing. Most of these missing bands overlap with those of the groups either preceding or following their own, and so it may be that their presence is masked by the others. It is possible, however, to explain their absence in the light of the present theory in a different way.

Each band involves a change between two orbits, one unstable and the other comparatively stable. According to the nature of the stimulus a molecule receives, the constituent atoms are raised to different unstable orbits. If a molecule receives high stimulus, a greater number of unstable orbits are created, and at the same time its stable orbits correspond to partially dissociated states of higher order. If it receives low stimulus, the higher members of the unstable orbits are not at all formed, and the stable orbits correspond to dissociated states of lower order.

Consequently, for higher quantum changes (higher stimulus) bands corresponding to lower orbits (*i. e.*, less dissociated states) are not observed, and for lower quantum changes (less stimulus) bands corresponding to higher orbits (*i. e.*, more dissociated states) are also not observed. In the discharge-tube, even under ordinary conditions, different molecules receive different degrees of stimulus, and that is why we find so many groups corresponding to lower as well as higher quantum changes. With the gradual increase of stimulus in the discharge, it is evident that molecules in the higher states of dissociation will be more numerous; consequently the intensity distribution in groups of higher values of n (quantum change) will have its maximum moving towards higher values of m (higher dissociated states). No actual experiment is on record to test this view, but the general distribution of intensity in the successive groups under ordinary conditions of discharge roughly points to the same conclusion. In fig. 1 (Pl. XIV.) the maximum of intensity for the *c* group corresponds to $m=5$ ($\lambda 6544.89$), for the *d* group at $m=7$ ($\lambda 5854.40$), and for the *e* group at $m=8$ ($\lambda 5372.82$).

The groups corresponding to quantum changes of 7 and upwards have not been collected in Table II. They overlap with the second positive bands, which are far stronger. Besides, owing to high stimulus, molecules cannot be expected to remain in the lower states; consequently, under favourable condition only, the bands corresponding to the last one or two members may be expected in each group.

The Significance of the Afterglow Bands.

In the same way it is possible to understand the characteristic of the afterglow spectrum. Owing to the enormous concentration of energy in the development of the afterglow bands, the stable states of the molecules correspond to the higher dissociated states. Consequently, only the bands corresponding to these higher states alone are greatly intensified. Those corresponding to the lower states are either missing altogether or appearing in greatly reduced intensity. In all cases where the bands are developed in the afterglow this feature is very prominent.

In some cases, still higher dissociated states and a greater number of unstable orbits are created, with the consequent development of a larger number of bands towards the tail. The group of heads forming the CN band at $\lambda 4216$ has been roughly arranged in series by the equation :

$$\nu = \nu_0 + 116m - 8m^2.$$

The values of the coefficients of m and m^2 having opposite signs, the series turn back after certain values of m ($m=7$), with the result that there is a crowding of several heads (about 7) in the small region between $\lambda 4143$ and $\lambda 4153$. Assuming, as has been suggested above, that a greater number of heads appear in the afterglow spectrum than in the ordinary arc, one would expect a crowding of lines at the tail. The cyanogen bands developed by acetylene in the afterglow of active nitrogen by Fowler and Strutt* fully confirm this view.

Infra-red Absorption corresponding to the Emission of the First Positive Bands.

In the theoretical section, in connexion with equation (5) it has been mentioned that the value of the coefficient B' is of the same order of magnitude as a' , the natural frequency of vibration of the atom, and that D approximately determines

* A. Fowler and R. J. Strutt, Proc. Roy. Soc. A, lxxxvi. (1912).

the change in α' due to a change in the quantum states. The positive value of D , as obtained in equation (6), therefore suggests that the natural frequencies in the higher dissociated states are gradually decreasing numbers, the frequency in the state order number m being expressed as $B' - mD$. As the atoms are expected to absorb most readily the waves which correspond to their own natural frequency, the waves corresponding to the numbers $B' - mD$ will be strongly absorbed. Besides these there will be a comparatively weaker absorption of the waves corresponding to the upper harmonics of the free vibrations of the atoms in the different states. Consequently the general equation, giving the absorption in the infra red, will be of the form $n(B' - mD)$, m and n having successive integral values.

The absorption bands of nitrogen in the infra red are not on record, but Coblenz* has made a study of the infra-red emission from discharge-tubes containing nitrogen. Besides the sharp maximum at 1.06μ mentioned before, he observed noticeable deflexions in the region between 4.8 to 6.5μ , without any sharp maximum anywhere. This would therefore correspond to a series of radiations with small differences in their frequencies. The calculated frequency corresponding to B' in equation (6) is 5.73μ . The emission corresponding to the vibrations of the atoms in the different dissociated states, given by the equation $B' - mD$, therefore closely agrees with those described by Coblenz. It would, however, be very interesting to test whether the absorption bands of nitrogen are actually found in this region or not.

Correlation with the Ionization Potential Experiments in Nitrogen.

It has been suggested in the theoretical section that corresponding to the successive higher values of m the molecule is in gradually higher states of dissociation, so that the maximum of energy that can be radiated would correspond to a return of the atom from the limiting orbit to its primary orbit (i. e., $m=0$). Owing to the superposition of the bands of the second group, and also owing to the experimental difficulties attended with the production of such higher orbits, the corresponding radiation has not been recorded. But it is possible to calculate it indirectly. The bands in the first column are seen to slowly converge; clearly the maximum radiation would correspond to the convergence

* *Loc. cit.*

frequency. Since the heads of the groups may be calculated by the equation

$$\nu = 9244.8 + 1748.2n - 14.5n^2,$$

ν is maximum, given by $\frac{\partial \nu}{\partial n} = 0$; i. e., for $n = \frac{1748.2}{2 \times 14.5} = 60$.

Thus $\nu_{\max} = 61936.8$, which corresponds to the energy acquired by an electron falling through a potential difference V , where V in volts is given by the quantum relation

$$\frac{eV}{300} = h\nu; \therefore V = 7.6 \text{ volts.}$$

By the ionization potential experiments of Franck and Hertz, Brandt*, experimenting with nitrogen, has recorded a number of notches in his photo-electric curve which, when converted to the wave-length scale, correspond to bands identical in structure with the first positive bands of nitrogen. The potential corresponding to this ionization is 7.9 volts. It is clear that the ionization current cannot be due to the liberation of electrons by a complete dissociation of the molecules, for this would entail the ionization of at least one of the constituent atoms, which for nitrogen atom is much higher. It is, however, likely that the photo-electric currents are due to the ionization of the nitrogen by the ultra-violet radiation of the extended series of the first positive bands corresponding to the limiting orbits. The remarkably close agreement with the calculated value indicates that there may be some truth in the above suggestion.

The cases of other complicated bands—for example, the second positive bands of nitrogen, the negative bands of nitrogen, and the red cyanogen bands—have also been studied. They all show satisfactory agreement with the formula deduced.

SUMMARY.

1. On the basis of Heurlinger and Lenz's equation for the band spectra, three different equations have been obtained which may express the relation between the characteristic frequencies in a system of bands.

2. The case of the most complicated system has been studied in detail with reference to the first positive bands of nitrogen. Their series equation has been obtained, and it

* Brandt, *Berliner dissertation*. See Franck, *Phys. Zeit.* xxii, pp. 388, 409, 441, 466 (1921).

shows perfect similarity with the equation theoretically deduced.

3. The significance of the afterglow bands has been discussed in the light of the theory.

4. From the data available from a study of the emission bands, the character of the infra-red absorption bands has been discussed.

5. A possible method of correlation with the ionization potential experiments in nitrogen has been suggested.

DESCRIPTION OF THE PLATE.

First positive bands of Nitrogen.

I. Scheme adopted in the present paper.

II. " " by Cuthbertson.

III. " " " Von der Helm.

LXIX. *Some Problems of Two-Dimensional Electrostatics.*

By D. M. WRINCH, *B.Sc.*, *Lecturer at Lady Margaret Hall, Oxford* *.

SUMMARY.

THIS paper treats electrical problems relating to infinite cylindrical conductors whose curves of cross-section are of the form

$$\left. \begin{aligned} x &= na \cos t + b \cos nt \\ y &= na \sin t - b \sin nt \end{aligned} \right\}, \dots \dots \dots (1)$$

with n any positive integer and b not greater than a . This class of curves depending on three parameters a , b , and n is of considerable generality and comprises the closed nodeless epicycloids of retrograde type sometimes also called hypotrochoids, which are among the curves traced out by a point whose motion is compounded of two uniform circular motions in opposite senses. They exhibit the phenomena of convexities and concavities and outward pointing cusps.

By means of the complex variable w , defined by the relation

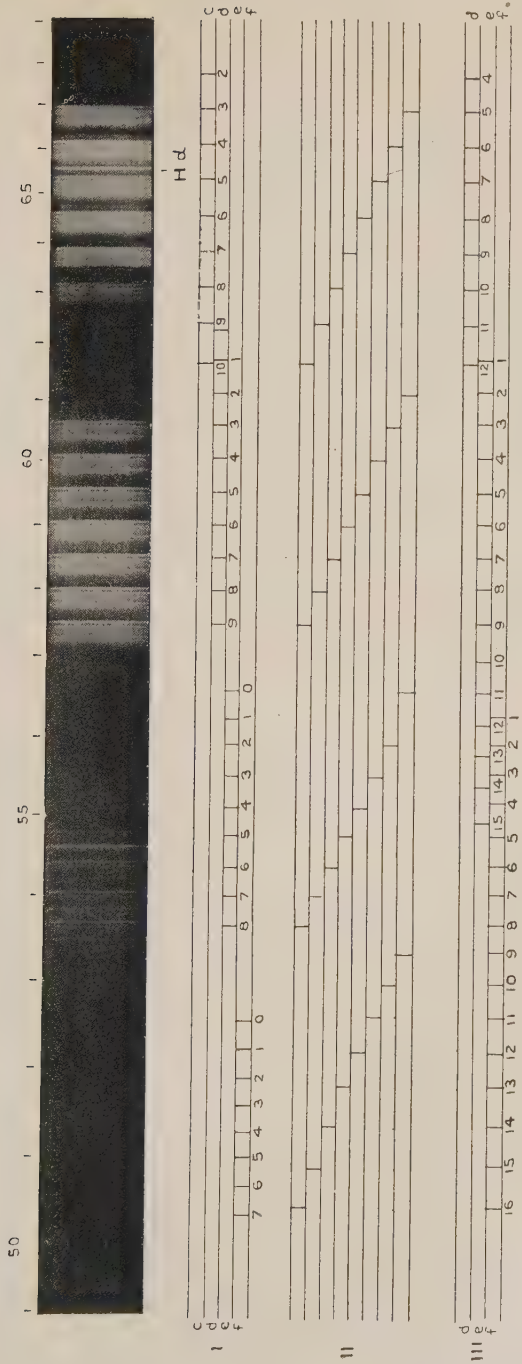
$$z = na e^{iw} + b e^{-niw},$$

the problem of a freely charged cylinder of type (1) is solved and the surface density of electrification at any point of the cylinder specified by the parameter t or the radius vector r is given by

$$\begin{aligned} 4\pi\sigma &= 2e/|ds/dt| \\ &= 2e/n(a^2 + b^2 - 2ab \cos(n+1)t)^{\frac{1}{2}} \\ &= 2e/n^{\frac{1}{2}}(n+1)(na^2 + b^2 - r^2)^{\frac{1}{2}} \end{aligned}$$

if e is the charge on the cylinder per unit length. This result in the

* Communicated by the Author.



I = Datta. II = Cuthbertson. III = Von der Helm.

special cases when a and b are equal and the curve of cross-section is cusped is exhibited also in the form

$$4\pi\sigma = (n-1)e/np,$$

where p is the perpendicular from the centre on the tangent to the curve of cross-section at the point. It presents an interesting contrast to the result for the cylinder of elliptic cross-section

$$4\pi\sigma = 2ep/(a^2 - b^2).$$

In the course of this investigation, it is found that all the hypotrochoids (a, b) of any specific positive integral order n , for which $a^n b$ has a constant value, form a set of equipotentials, in the sense that if the cylinder whose cross-section is any one of them is freely electrified, the equipotentials are the cylinders external to it whose cross-sections are the other members of this set. This result provides a wide generalization of the equipotential character of sets of confocal ellipses. This fact allows the solution of the problem of the condenser formed by two cylinders $(a_1 b_1 n)$ $(a_2 b_2 n)$ of type (1) in the case when $a_1^n b_1 = a_2^n b_2$. Its capacity is found to be

$$1/(2 \log (a_2/a_1))$$

per unit length.

An investigation is also included of the electrification of a cylinder of type (1) when insulated in a uniform field of electric force. If the strength of the field is f and if the lines of force in the undisturbed field make an angle α with the axis of x , the surface density is given by

$$4\pi\sigma = 2fa \cos (t - \alpha) / (a^2 + b^2 - 2ab \cos (n+1)t)^{\frac{1}{2}}.$$

Introduction.

THE problem of the electrification of cylindrical conductors of infinite length has been solved in a variety of cases. In each case the fundamental problem is the electrification when the conductor is freely charged. When this has been solved it is in general possible to treat the conductor placed in any electric field, whether the field is expressed as a general law—as, for example, the uniform field—or as the effect of a system of discrete line charges or doublets outside the conductor.

The solution of two-dimensional electrostatic problems has so far been accomplished mainly by the use of the principle of conformal transformation. This method has permitted the solution of a few simple cases, notably the case when the curve of cross-section of the cylinder is an ellipse or a hyperbola, and of a wide variety of isolated cases when the curve of cross-section is, for example, a rectangle or a circular arc or an equilateral triangle. The solution when the curve of cross-section is an ellipse or a hyperbola is of fundamental importance on account of the fact that the equipotentials associated with an elliptic or hyperbolic

cylinder when it is freely charged are the elliptic or hyperbolic cylinders confocal with it and external to it. The solution in this case, in fact, shows that a family of confocal ellipses—and equally a family of confocal hyperbolæ—forms a set of equipotentials in the sense that a freely charged cylinder whose curve of cross-section is any member of the family has as its equipotentials the cylinders external to it, whose curves of cross-section are the other members of the family. And the great importance of the solution of the elliptic and hyperbolic cylinders is, indeed, due to the fact that the equipotential set to which an ellipse belongs is the family of confocal ellipses, and that the equipotential set to which a hyperbola belongs is the family of confocal hyperbolæ.

It has therefore been deemed worth while to call attention, in this paper, to certain families of simple curves which form sets of equipotentials and to submit the solution of the fundamental problem of the corresponding cylinders when they are freely charged and of the most important of the subsidiary problems, the problem of the induction in a uniform field of force. Certain types of condensers are also considered.

The curves are of algebraic type and include the ellipse and hyperbola as a special case. We refer to the closed nodeless epicycloids of integral order n of retrograde type, defined in terms of a parameter in the form

$$\begin{aligned} x &= na \cos t + b \cos nt, \\ y &= na \sin t - b \sin nt, \end{aligned} \quad (b \leq a).$$

where the product $a^n b$ is constant, and to their orthogonal trajectories. These epicycloids are easily visualized as the paths of points whose motion is compounded of two uniform circular motions. They also present themselves in another manner as the path traced out by a point on a circle which rolls in inside contact with a fixed circle and are called in this connexion hypotrochoids. This curve becomes the ellipse when n is unity, and is familiar when n is three and a and b are equal as the astroid. The radius vector of the curve r , given by

$$r^2 = n^2 a^2 + b^2 + 2nab \cos (n+1)t,$$

is periodic in $2\pi/(n+1)$: the curve consequently consists of $(n+1)$ similar arcs symmetrically oriented. When a and b

are equal, the curve is star-shaped with $(n + 1)$ cusps; otherwise it has continuous curvature*.

Fig. 1 shows specimens of the curves under discussion.

The fact that the curves treated in this paper possess points of inflexion, concave and convex arcs and cusps lends special interest to the solutions of the cylindrical conductors with these curves as cross-section. They give, in fact, interesting and comprehensive information as to the effect of curvature on the distribution of electricity on conductors, at the same time giving exact quantitative information in a wide and representative class of cases.

In a recent paper† H. W. Richmond has used the Schwarz-Christoffel transformation to obtain the solution of the two-dimensional electrostatic problems when the curve

Fig. 1.



of cross-section of the cylinder is made up of segments of any ellipses belonging to one confocal system and of their orthogonal trajectories, and his interesting adaptation of the transformation applied to any specific set of curves which form a set of equipotentials gives the solution when the cross-section of the cylinder is made up of segments of curves belonging to this set and to the set of their orthogonal trajectories. The set of equipotentials obtained in this paper can be used in the same way as the confocal ellipses, and a wide variety of curves of cross-section can be treated by taking curves made up of segments of any of the hypotrochoids belonging to one set of equipotentials and their orthogonal trajectories.

* A discussion of the geometrical properties of these curves is given by Lamb, 'Infinitesimal Calculus,' pp. 297-307 (1919). The curves are easily described mechanically with a lathe; a number of interesting diagrams obtained in this manner are reproduced in R. A. Proctor's 'Treatise on the Cycloid and Cycloidal Curves' (1878), which also contains an exhaustive account both of the history and of the geometrical properties of these curves.

† Proc. Lond. Math. Soc. (2) xxii. pp. 483-494 (1924).

I. *Freely Charged Cylinders.*

The equation of c the curve of cross-section of the cylinder is taken in the parametric form

$$\begin{aligned}x &= x(t) = na \cos t + b \cos nt \\y &= y(t) = na \sin t - b \sin nt\end{aligned}\quad (1)$$

with n a positive integer and b not greater than a . The radius vector from the centre of the curve is given by

$$r = r(t) = (n^2 a^2 + b^2 + 2nab \cos (n+1)t)^{\frac{1}{2}}.$$

The radius vector of the curve is therefore periodic in $2\pi/(n+1)$ as a function of t : the curve, in fact, consists of $(n+1)$ arcs symmetrically oriented about the centre, which is the centre of coordinates, and each of these arcs lies partly inside and partly outside the fundamental circle of radius na . The arc of the curve, s , is given by the equation

$$\begin{aligned}\dot{s} &= (ds/dt)^2 = \dot{x}^2 + \dot{y}^2 \\&= n^2(a^2 + b^2 - 2ab \cos (n+1)t) \\&= n((n+1)(na^2 + b^2) - r^2).\end{aligned}$$

Further, the perpendicular from the centre on the tangent to the curve at any point t is given by

$$\begin{aligned}p^2 &= (x\dot{y} - y\dot{x})^2 / \dot{s}^2 \\&= \frac{(na^2 - b^2 - ab(n-1) \cos (n+1)t)^2}{[a^2 + b^2 - 2ab \cos (n+1)t]},\end{aligned}$$

or in terms of r , by the equation

$$p^2 = \frac{((n+1)(n^2 a^2 - b^2) - (n-1)r^2)^2}{4n[(n+1)(na^2 + b^2) - r^2]},$$

so that when a is equal to b , the (p, r) equation has the simple form

$$4np^2 = (n-1)^2((n+1)^2 a^2 - r^2),$$

and becomes, when n is unity,

$$p^2 = (a^2 - b^2)^2 / (2a^2 + 2b^2 - r^2),$$

the (ρ, r) equation for the ellipse with semi-axes $(a+b)$ and $(a-b)$. The curvature c is given by

$$\begin{aligned}c = 1/\rho &= (x\dot{y} - y\dot{x})/s^3 \\&= \frac{a^2 - nb^2 + (n-1)ab \cos (n+1)t}{n(a^2 + b^2 - 2ab \cos (n+1)t)^{\frac{3}{2}}}.\end{aligned}$$

When b is zero the curve becomes the circle and is everywhere concave to its centre. In the other extreme case,

when a and b are equal, the curve becomes the cusped hypocycloid and is everywhere convex to the origin. In the intermediate cases (the case $n=1$ excepted), if the ratio b/a is sufficiently small, the curve is everywhere concave to the origin. For larger values of this ratio each arc of the curve is partly concave and partly convex, with the limiting case when b and a are equal as the only case in which the curve is wholly convex.

The equation of c , the curve (1), may be written in the form

$$z=x+iy=nae^{it}+be^{-nit}.$$

The complex variable

$$w=u+iv$$

is now introduced by the relation

$$z(w)=x(w)+iy(w)=nae^{iw}+be^{-niw}.$$

When $v=0$ z lies on the curve c with u equal to the parameter t . Also when $v=-\infty$, z lies on the circle at infinity, with u equal to the argument of z . Finally

$$dz/dw=in(ae^{iw}-be^{-niw}),$$

and this is infinite only when $v=-\infty$, and zero only when

$$(n+1)v=\log(a/b)\geq 0, \cos(n+1)t=1.$$

When b and a are equal and the curve is cusped, those points at which dz/dw is zero lie on the curve at the cusps, otherwise they lie inside the curve. Consequently for points between the curves $v=0$ and $v=-\infty$, dz/dw is never infinite and never zero.

Using the variable w , we may now introduce the W -function

$$W=U+iV,$$

where V is the potential and U the corresponding conjugate function, given by

$$iW=iU-V=2eiw+\text{constant}.$$

Then, on the curve c , which has been shown to be given by $v=0$, V is constant. On the circle at infinity, which it will be convenient to call the curve C ,

$$V+2e\log r=\text{constant}.$$

Further, between the curves c and C , V has no singularities. These considerations are sufficient to show that V is the potential of the cylinder whose cross-section is the curve c , when it bears a charge e per unit length.

The surface density σ , at any point t of the curve, is then given by

$$\begin{aligned} 4\pi\sigma &= 2e |dw/dz| = 2e |ds/dt| \\ &= 2e/n(a^2 + b^2 - 2ab \cos(n+1)t)^{\frac{1}{2}}, \end{aligned}$$

or, in terms of the radius vector,

$$4\pi\sigma = 2e/(n(n+1)(na^2 + b^2) - nr^2)^{\frac{1}{2}}.$$

Thus the surface density is a maximum at the points at which r is greatest and a minimum at the points at which r is least, ranging in fact from the maximum value

$$e/2\pi n(a-b)$$

to the minimum value

$$e/2\pi n(a+b).$$

The special case when n is unity represents the ellipse with semi-axes $(a+b)$ and $(a-b)$ and yields the well-known result

$$\begin{aligned} 4\pi\sigma &= 2e/(2a^2 + 2b^2 - r^2)^{\frac{1}{2}} \\ &= 2ep/(a^2 - b^2). \end{aligned}$$

In the particular case of the hypocycloids—the cusped curves which result when a and b are equal—,

$$\begin{aligned} 4\pi\sigma &= e/na |\sin \frac{1}{2}(n+1)t| \\ &= (n-1)e/np. \end{aligned}$$

The surface density is in fact infinite at all the $(n+1)$ cusps and decreases to the value $e/4\pi na$ at the intermediate points.

It is interesting to notice the contrast afforded by these two particular cases: the ellipse with the law $\sigma \propto p$ being wholly concave to the origin and the cusped hypocycloids with the law $\sigma \propto 1/p$ being wholly convex.

II. *Cylindrical Condensers.*

In the case of a cylinder whose cross-section c has the parametric equation (1), the complex variable w given by

$$z = na e^{iw} + b e^{-niw} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is introduced, and the W -function is taken in the form

$$iW = iU - V = 2eiw + \text{constant}.$$

The equipotentials associated with the freely charged cylinder are consequently cylinders whose cross-sections are

the v -levels of the function (2), being given by the equation

$$\begin{aligned}x &= nae^{-v} \cos u + be^{nv} \cos nu \\y &= nae^{-v} \sin u - be^{nv} \sin nu\end{aligned}$$

for values of v between zero and $-\infty$. Thus for example, the equipotentials associated with the curve

$$\begin{aligned}x &= k(n \cos u + \cos nu) \\y &= k(n \sin u - \sin nu)\end{aligned}$$

—which is the hypocycloid with $(n+1)$ cusps—are the set of hypotrochoids

$$\begin{aligned}x &= na \cos u + b \cos nu \\y &= na \sin u - b \sin nu,\end{aligned}$$

in which $a^n b = k^{n+1}$.

Any two hypotrochoids with parameters a_1 and b_1 , a_2 and b_2 are therefore represented by two constant values of v , say v_1 and v_2 , in the transformation

$$z = k(ne^{iv} + e^{-niw}),$$

provided that $a_1^n b_1 = a_2^n b_2$,

the actual values of k , v_1 , and v_2 being given by

$$k^{n+1} = a_r^n b_r, \quad v_r = \log(k/a_r). \quad (r=1, 2)$$

Thus we can at once find the capacity of a condenser consisting of two cylinders whose curves of cross-section are these two hypotrochoids. For if V_1 and V_2 are their potentials, we evidently have, for the potential in the region between them,

$$V = 2ev + \text{constant},$$

if the inner cylinder (a, b) has a charge e per unit length, and

$$V_1 - V_2 = 2e(v_1 - v_2) = 2e \log(a_2/a_1).$$

The capacity is consequently seen to be

$$1/(2 \log(a_2/a_1))$$

per unit length. It may be remarked that the capacity of the condenser in this case is identically equal to the capacity of two circular cylinders whose cross-sections are the fundamental circles of radius na_1 and na_2 associated with the hypotrochoids.

And it is worthy of notice that the set of hypotrochoids (a, b) of any specific positive integral order n form an equipotential set, so long as $a^n b$ has a constant value, the

innermost member of such an equipotential set being the hypocycloid with $(n+1)$ cusps. These results will be seen to provide a wide generalization of the equipotential character of sets of confocal ellipses, which on this occasion present themselves in the unwonted aspect of hypotrochoids, the innermost member of the family, the straight line ellipse, being only with difficulty recognized under the elaborate designation of the "two-cusped hypocycloid."

Fig. 2 gives a sketch of the hypotrochoids of order three which form a set of equipotentials.

Fig. 2.



III. *Cylinders in a Uniform Field.*

Suppose the cylinder c with cross-section

$$x = na \cos t + b \cos nt$$

$$y = na \sin t - b \sin nt$$

is placed in a uniform field of electric force given by

$$iW_0 = f_0 + fze^{-i\alpha},$$

so that

$$-V_0 = f_0 + f(x \cos \alpha + y \sin \alpha),$$

$$U_0 = f(y \cos \alpha - x \sin \alpha).$$

Let

$$iW_1 = iU_1 - V_1$$

represent the disturbance due to the presence of the cylinder, and let

$$iW = iU - V$$

be the W -function for the field when the cylinder is present, so that

$$iW = iW_0 + iW_1.$$

The conditions of the problem will be satisfied if V_1 is a solution of Laplace's equation evanescent on the circle at infinity and such that $V_0 + V_1$ is constant on the curve c , having no singularities in the region between the circle at infinity and the curve c .

We again use the complex variable w defined by the relation

$$z = nae^{iw} + be^{-niw},$$

so that $v=0$ is the curve c with $u=t$ and $v=-\infty$ is the circle at infinity. Then in terms of w ,

$$iW_0 = f_0 + f(nae^{iw-ia} + be^{-niw-ia}),$$

so that

$$-V_0 = f_0 + f(nae^{-v} \cos(u-\alpha) + be^{nv} \cos(nu+\alpha)).$$

Then put

$$-V_1 = -f(nae^v \cos(u-\alpha) + be^{nv} \cos(nu+\alpha)),$$

and consequently

$$iW_1 = -f(nae^{-iw+ia} + be^{-niw-ia}),$$

for then

$$iW = f_0 + 2niaf \sin(w-\alpha),$$

$$-V = f - 2naf \cos(u-\alpha) \sinh v,$$

$$U = 2naf \sin(u-\alpha) \cosh v,$$

which makes V , on the curve c , equal to $-f$, the potential at the centre of the curve in the undisturbed field: and V_1 is evanescent on $v=-\infty$ and without singularities between c and the circle at infinity.

The surface density σ at any point t is given by

$$4\pi\sigma = 2fa \cos(t-\alpha) / (a^2 + b^2 - 2ab \cos(n+1)t)^{\frac{1}{2}}.$$

The total amount of electricity separated on the cylinder per unit length is evidently nfa/π , the amount separated per unit length on a circular cylinder of radius na .

The solution for the hypocycloidal cylinders—for which a and b are equal—is of special interest. We have

$$4\pi\sigma = f \cos(t - \alpha) / |\sin \frac{1}{2}(n+1)t|.$$

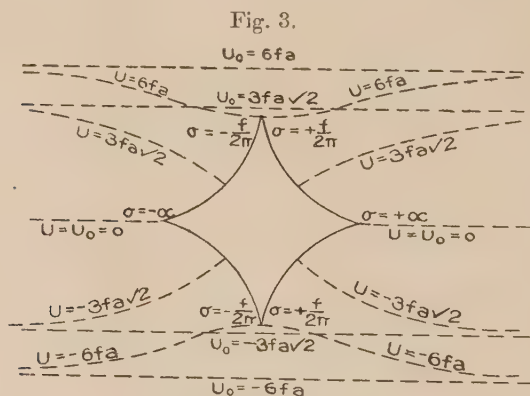
In general, therefore, there will be infinities for σ at the $(n+1)$ cusps, the sign of these infinities being determined by the sign of $\cos(t - \alpha)$. If, however, the field is perpendicular to the tangent at a cusp t_0 , so that $\cos(t_0 - \alpha)$ vanishes, the infinity for σ at this cusp will disappear and instead there will be a jump in the value of σ from the value

$$\sigma = -\frac{1}{2}f/(n+1)\pi$$

at the point $t = t_0 - 0$, to the value

$$\sigma = +\frac{1}{2}f/(n+1)\pi$$

at the point $t = t_0 + 0$. Thus there will either be infinities at all the $(n+1)$ cusps: or when n is odd, infinities at n cusps



and a discontinuity at a single cusp, and when n is even, infinities at $(n-2)$ cusps and discontinuities at two diametrically opposite cusps. Fig. 3 shows the distribution of electricity and the lie of the lines of force in the case of the astroid ($n=3$) when the field is along an axis of the curve and there are consequently infinities at the two cusps on this axis and discontinuities at the other two cusps.

IV. *Application of the Schwarz-Christoffel Transformation.*

By means of an adaptation of the Schwarz-Christoffel transformation, the solution is obtained of the electrostatic

problems relating to a cylinder whose curve of cross-section is made up of segments of the hypotrochoids

$$x = na \cos t + b \cos nt,$$

$$y = na \sin t - b \sin nt,$$

with a^nb equal to some constant, say k^{n+1} , and their orthogonal trajectories. For with the transformation

$$z = k(ne^{iw} + e^{-uw})$$

such a curve of cross-section is represented in the w -plane by segments of lines parallel to the axes of u and v ; to such a curve the Schwarz-Christoffel method can at once be applied. The solutions of two-dimensional electrostatic problems are therefore available in a very wide set of subsidiary cases and can easily be worked out by means of a double transformation, if they are required. It is unnecessary to point out the fact that these solutions—in marked contradistinction to the solutions for cylinders of hypotrochoidal cross-section given in this paper—are by no means suitable for practical application, since they involve, in general, integrals of complicated elliptic and hyperelliptic type*.

LXX. *The Critical Pressure-Ratio for Gases as affected by Variable Specific Heat.* By W. J. WALKER, Ph.D., University College, Dundee †.

Summary.

IN a previous paper in the 'Philosophical Magazine' for March 1922, the analysis involving the effect of variable specific heat on the discharge of gases through orifices or nozzles was given, and certain important conclusions were drawn therefrom. In the present note the critical pressure-ratio determining the maximum discharge condition under variable specific heat conditions has been deduced. The

* Reference should be made to the paper by H. W. Richmond already cited. Results are there obtained by reference to confocal ellipses and their orthogonal trajectories, the confocal hyperbolæ, in virtue of the equipotential character of these families of curves. By reference to the sets of hypotrochoids, whose equipotential character is demonstrated in this paper, and their orthogonal trajectories, powerful generalizations of these results may be obtained.

† Communicated by the Author.

result obtained shows that this critical pressure-ratio is higher the higher the temperatures involved, and is also higher than under constant specific heat conditions.

Under adiabatic conditions of flow from a region of higher pressure p_1 to one of lower pressure p_2 , the velocity of flow of a gas is given by

$$u_2^2 - u_1^2 = 2g(I_1 - I_2), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

u denoting velocity in feet per second, and I denoting total heat energy in ft.-lb. per lb. The total heat-energy change involved in giving the gas this kinetic energy during expansion is

$$= \int_{T_2}^{T_1} dI = \int_{T_2}^{T_1} v dp,$$

v denoting specific volume in cubic ft. per lb., and p denoting pressure in lb. per sq. ft.

To a first and close approximation this may be written

$$I_1 - I_2 = \left(\frac{p_1 v_1 - p_2 v_2}{m-1} \right) \left\{ 1 + \frac{\lambda}{2R} (p_1 v_1 + p_2 v_2) \right\} + p_1 v_1 - p_2 v_2,$$

λ being small in relation to other factors and having the same signification as in previous papers.

$$\begin{aligned} \therefore I_1 - I_2 &= \frac{m}{m-1} \left\{ p_1 v_1 - p_2 v_2 \right\} \left\{ 1 + \frac{\lambda}{2mR} (p_1 v_1 + p_2 v_2) \right\} \\ &= \frac{mR}{m-1} \left\{ T_1 - T_2 \right\} \left\{ 1 + \frac{\lambda}{2m} (T_1 + T_2) \right\}. \quad . \quad . \quad (2) \end{aligned}$$

Now, the velocity of sound in a gas under specific volume v and pressure p is given by

$$\begin{aligned} C &= \sqrt{\frac{K}{K_p} g p v}, \\ &= \sqrt{m g r p} \left\{ 1 - \lambda T \left(\frac{m-1}{m} \right) \right\} \text{ to a first and close approximation,} \\ &= \sqrt{m g R T} \left\{ 1 - \lambda T \left(\frac{m-1}{m} \right) \right\}. \quad . \quad . \quad . \quad . \quad (3) \end{aligned}$$

Assuming, as is usually very nearly true under most practical conditions, that u_1 is negligible in relation to u_2 , then equations (1), (2), and (3) combined give

$$u_2^2 = \frac{2}{m-1} \left\{ C_1^2 - C_2^2 \right\} \left\{ 1 + \frac{\lambda(2m-1)}{2m} (T_1 + T_2) \right\}. \quad . \quad (4)$$

Now, the critical pressure-ratio must, just as under constant specific heat conditions, be that producing a gas-discharge velocity equal to the velocity of sound through the gas under the conditions prevailing at the discharge side. From (4), therefore, since $u_2 = C_2$ at the critical pressure-ratio,

$$\begin{aligned} u_2^2 \left\{ 1 + \frac{m-1}{2} + \frac{\lambda(2m-1)}{2m} (T_1 + T_2) \right\} \\ = C_1^2 \left\{ 1 + \frac{\lambda(2m-1)(T_1 + T_2)}{2m} \right\}; \\ \therefore T_2 \left\{ 1 - \lambda T_2 \left(\frac{m-1}{m} \right) \right\} \left\{ 1 + \frac{m-1}{2} + \frac{\lambda(2m-1)}{2m} (T_1 + T_2) \right\} \\ = T_1 \left\{ 1 - \lambda T_1 \left(\frac{m-1}{m} \right) \right\} \left\{ 1 + \frac{\lambda(2m-1)(T_1 + T_2)}{2m} \right\}; \\ \therefore \frac{m+1}{2} T_2 \left[1 - \lambda T_2 \left\{ \frac{(m-1)}{m} - \frac{(2m-1)(m+3)}{2m(m+1)} \right\} \right] \\ = T_1 \left[1 - \lambda T_2 \left\{ \frac{(m-1)(m+1)}{2m} - \frac{(2m-1)(m+3)}{4m} \right\} \right]; \\ \therefore \frac{m+1}{2} T_2 = T_1 \left\{ 1 + \lambda T_2 \frac{(5m-1)(m-1)}{4m(m+1)} \right\}. \quad \dots \quad (5) \end{aligned}$$

But, under adiabatic conditions of flow,

$$\begin{aligned} \frac{p_2}{p_1} &= \left(\frac{T_2}{T_1} \right)^{\frac{m}{m-1}} e^{\frac{\lambda(T_2 - T_1)}{m-1}}, \\ &= \left(\frac{T_2}{T_1} \right)^{\frac{m}{m-1}} \left\{ 1 + \frac{\lambda(T_2 - T_1)}{m-1} \right\} \quad \text{to a first and close approximation,} \\ &= \left(\frac{T_2}{T_1} \right)^{\frac{m}{m-1}} \left\{ 1 - \frac{\lambda T_2}{2} \right\}. \end{aligned}$$

Therefore from (5)

$$\frac{p_2}{p_1} = \left(\frac{2}{m+1} \right)^{\frac{m}{m-1}} \left\{ 1 + \frac{3\lambda T_2(m-1)}{4(m+1)} \right\}. \quad \dots \quad (6)$$

Under constant specific heat conditions the critical ratio is usually given as

$$\frac{p_2}{p_1} = \left(\frac{2}{\gamma+1} \right)^{\frac{\gamma}{\gamma-1}},$$

where $\gamma = \frac{K_p}{K_v}$.

The term in double brackets in (6) therefore represents the effect due to variable specific heat.

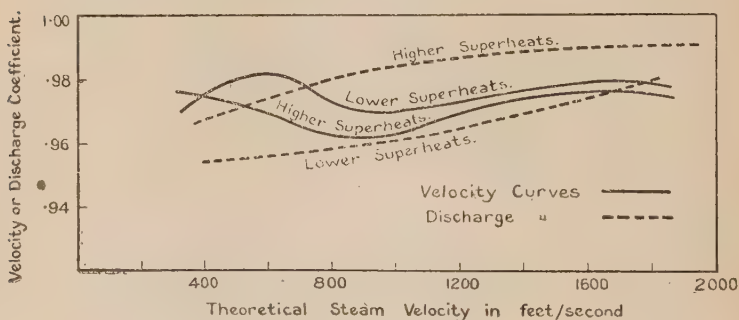
The inferences to be drawn from (6) are that the critical pressure-ratio

- (1) Varies as the temperature is altered, and
- (2) Diminishes or increases according to whether the specific heat of the gas diminishes or increases respectively with rise of temperature.

It should be noted that at normal temperatures the value of the term

$$\frac{3\lambda T_2(m-1)}{4(m+1)}$$

is practically negligible. Thus for an average internal combustion engine working fluid, $\lambda = 0.00283$ approx. when T is in $^{\circ}\text{C. absolute}$. Taking $T_2 = 288^{\circ}\text{C. absolute}$, the value of the term becomes 0.0102 when m is assumed equal to 1.4 . At the higher temperatures, however, it may have quite appreciable values.



It may reasonably be claimed that the formulæ thus derived, as given by the writer in this and previous papers, give very close approximation to the actual effect of variable specific heat. This is borne out by the following further recent remarkable verification of the formulæ given in the previous paper in the 'Philosophical Magazine,' March 1922.

In the Third Report of the Steam Nozzles Research Committee, published in the 'Proceedings of the Institution of Mechanical Engineers,' May 1924, the velocity and discharge coefficient curves, reproduced here in the diagram, are published. The experiments from which these curves have been derived have been carried out under conditions conducive to the highest accuracy, and there is no reason to doubt their validity.

Both the velocity and discharge coefficients for these curves

have been calculated from the tests by the application of Callendar's equations, and, as will be observed from the figure, the velocity and discharge curves occupy reversed positions in relation to superheat. Since λ , for superheated steam, is negative within the experimental range concerned, this is exactly what should occur according to the writer's variable specific heat equations for velocity and discharge if variable specific heat is neglected or not sufficiently taken into account. Not only so, but in further conformity with these equations, which show that the percentage error due to neglect of variable specific heat in calculating the discharges will be three times the error made in calculating the velocities, it will be observed from the reproduced curves that even this secondary result is verified, the difference between the dotted or discharge coefficient curves being decidedly more marked than that between the full line or velocity coefficient curves. This agreement can scarcely be accidental, and it does not appear possible that any valid argument based on friction effects or variation in coefficient of contraction can be adduced to nullify it.

LXXI. *On the Irregularity of the $L\alpha$ Doublet in the X-ray Spectra.* By B. B. RAY, D.Sc. (Lecturer, Calcutta University)*.

1. *Introduction.*

THE normal electronic arrangement about the nucleus, according to Bohr, should be such as would result from the capturing of electrons, one at a time, by the structure, each electron occupying that orbit which is most stable with respect to the nucleus and previously bound electrons. Following this scheme, one would find 2 electrons in the K-shell, 8 in the L-shell, 18 in the M-shell, and so on, in the elements of higher atomic numbers. The influence of a newly added electron in higher elements is very small, amounting practically to nothing in the innermost shells. If this view be accepted, then as one goes from lower to higher elements the influence of electrons in the outer shells should gradually decrease to zero in the K or L-shells. If the $K\alpha$ doublet, *i. e.* the difference in wave-length between $K\alpha_1$ and $K\alpha_2$, which is formed by the jumps of electrons from the L-shell to the K-shell, is examined from the lower to the higher elements, one would find that the gradual increase in $\Delta\lambda$ of the $K\alpha$ doublet is more rapid in the lower elements than the higher ones, and in the latter this value ($\Delta\lambda$) ultimately tends to be almost constant. But

* Communicated by Prof. Manne Siegbahn.

the newly added electron is not always added to the outermost shell, and there are regions where it goes rather to the inside shell, thus increasing the number in this shell, and forming a more stable arrangement; this we find in the elements from Ti (22) to Cu (29). In the former we have 4, 4, 2 electrons in the M-shell and 2 electrons in the N-shell, but in the latter we have 6, 6, 6 electrons in the M-shell and 1 in the N-shell. Thus in this arrangement, as the electrons in the L-shell are influenced by those of the next outer shell M, some changes are to be expected in the $K\alpha$ doublet in this region. So also in the elements from Al (13) to A (18). In a former paper, Siegbahn and the author* studied the $K\alpha$ doublet in these regions, and changes as expected from the Bohr scheme were actually found. It thus appeared that in the higher elements, where such changes should occur in the N-shell as expected by Bohr, the $L\alpha$ doublet would be affected, and by studying the doublet, such changes may be observed. According to Bohr the electrons are arranged in the following way and we quote them only from Y (39) to Th (90) as relevant to this paper.

${}_Z K.$	K.	L.	M.	N.	O.	P.	
Z.	1_1	$2_1 2_2$	$3_1 3_2 3_3$	$4_1 4_2 4_3 4_4$	$5_1 5_2 5_3 5_4 5_5$	$6_1 6_2 6_3 6_4 6_5 6_6$	$7_1 7_2$
39 Y	2	4 4	6 6 6	4 4 1	(2)		
40 Zr	2	4 4	6 6 6	4 4 2	(2)		
47 Ag	2	4 4	6 6 6	6 6 6	1		
48 Cd	2	4 4	6 6 6	6 6 6	2		
49 In	2	4 4	6 6 6	6 6 6	2 1		
54 X	2	4 4	6 6 6	6 6 6	4 4		
55 Cs	2	4 4	6 6 6	6 6 6	4 4	1	
56 Ba	2	4 4	6 6 6	6 6 6	4 4	2	
57 La	2	4 4	6 6 6	6 6 6	4 4 1	(2)	
58 Ce	2	4 4	6 6 6	6 6 6 1	4 4 1	(2)	
59 Pr	2	4 4	6 6 6	6 6 6 2	4 4 1	(2)	
71 Lu	2	4 4	6 6 6	8 8 8 8	4 4 1	(2)	
72 Hf	2	4 4	6 6 6	8 8 8 8	4 4 2	(2)	
79 Au	2	4 4	6 6 6	8 8 8 8	6 6 6	1	
80 Hg	2	4 4	6 6 6	8 8 8 8	6 6 6	2	
81 Tl	2	4 4	6 6 6	8 8 8 8	6 6 6	2 1	
86 Nt	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	
87 —	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	1
88 Ra	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	2
89 Ac	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4 1	(2)
90 Th	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4 2	(2)

* *Arkiv för Matematik, Astronomie och Fysik*, Band 18, No. 19.

From the above scheme the changes are to be expected from the elements Zr (40) to Ag (47) and Pr (59) to Lu (71).

2. Experimental Observations.

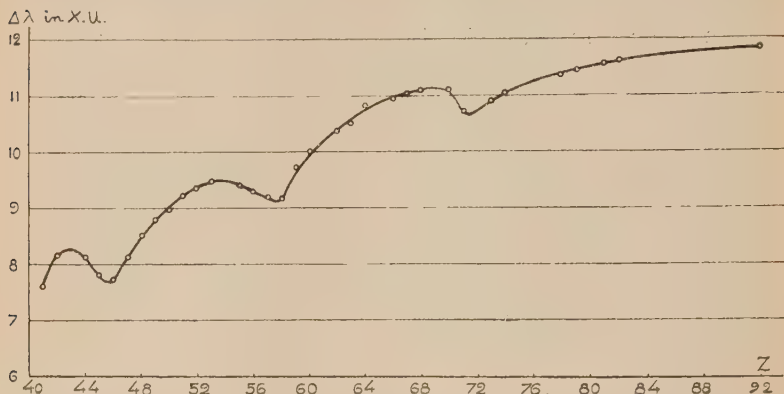
A Hadding tube was connected to an aluminium spectrograph, the width of the slit being 0.09 mm., and the photographic plate was placed at a distance of 12.15 cm. from the axis of the rotating face of the crystal. A current of 10 milliamp. at about 50 kilovolts was passed through the tube. The spectrograph was connected to an oil pump when vacuum was necessary within it. In the L α doublet, α_1 is a strong line and α_2 is rather weak, so that to get a good impression of α_2 , a rather long time (about 1 hour) is necessary, and this makes the strong line α_1 broad, thus increasing the error in the measurements of the distance between the lines. Several measurements are taken and the mean value of $\Delta\lambda$ is tabulated below. The values for Nb and Mo were kindly supplied by Mr. A. Larsson, and the value for U was taken from Siegbahn's table. Some plates were also taken in the higher order to check the result.

TABLE I.

Z.	$\Delta\lambda$ in X.U.	Z.	$\Delta\lambda$ in X.U.
41 Nb	7.58	60 Nd	10.05
42 Mo	8.23	62 Sm	10.35
44 Ru	8.15	63 Eu	10.50
45 Rh	7.78	64 Gd	10.81
46 Pd	7.72	66 Dy	10.95
47 Ag	8.16	67 Ho	11.02
48 Cd	8.51	68 Er	11.10
49 In	8.80	70 Yb	11.12
50 Sn	8.95	71 Lu	10.69
51 Sb	9.22	73 Ta	10.93
52 Te	9.40	74 W	11.02
53 I	9.48	78 Pt	11.39
55 Cs	9.42	79 Au	11.45
56 Ba	9.33	81 Tl	11.53
57 La	9.22	82 Pb	11.54
58 Ce	9.18	92 U	11.81
59 Pr	9.74		

A curve is also drawn with $d\Delta$ as ordinate and Z as abscissa.

From the figure it will be observed that the changes as expected from the Bohr model come out in a general way. As the α_1 line is rather broad it is necessary to examine whether the bends in the curve, especially in the regions Pd (46), Ce (58), and Lu (71), are due to experimental errors. In order to test this point, the highest values of $\Delta\lambda$ as measured from the plate in these elements were taken together with the smallest values of $\Delta\lambda$ in the elements Rh (45), Ag (47), Cs (55), Ba (56), Pr (59), Yb (70),



Ta (73), and W (74); it is found that the bends can still be seen as in fig. 1, thus proving the reality of the changes of the $L\alpha$ doublet in these elements.

3. Changes of α_1 and α_2 .

Some calculations are made in the $L\alpha$ doublet like those in the $K\alpha$ doublet, to determine whether the changes as observed in the figure may be due to the change of any one of them. But it is found that both the α_1 and α_2 lines undergo similar changes. In the ordinary relativity theory, α_1 (L series) results from the jump of an electron from the 3_3 orbit to the 2_2 orbit, whereas α_2 results from a jump from 3_2 to 2_2 . It is natural then to suppose on this view that α_2 should change more than α_1 , as the orbit 3_3 is circular and the orbit 3_2 is elliptical, and the influence of a newly added electron will be more felt by an elliptical orbit than by the circular one. But no such conclusion can be arrived at from our calculation. This result may be truly anticipated from the new suggestion about the formation of X-ray lines, just put forward by Landé*, whereby he assumes that

* *Zeit. f. Fys.* May 1924.

electrons in both the M_1 and M_2 -shell move in orbits of the same shape but different orientations.

My thanks are due to Prof. M. Siegbahn for suggesting the problem and taking keen interest during the progress of the work. My thanks are also due to Mr. R. Thoraeus and Mr. A. Larsson.

Physical Laboratory,
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LXXII. *The Mobility in Air of Ions produced in another Gas.*

By G. C. GRINDLEY, *B.Sc.*, and Professor A. M. TYNDALL, *D.Sc.**

WHILE many determinations of the mobility of gaseous ions have been made with a view to elucidating their nature, there is by no means unanimous agreement on the conclusions to be drawn from the results. Among some of the more interesting experiments may be classed those which deal with the mobility of ions formed in one gas and measured in another. Let us take for example the equation for mobility deduced from dynamical considerations by Langevin in 1905† :

$$K = \frac{.505}{\sqrt{P(K-1)}} \sqrt{1 + \frac{m}{M}},$$

where m = mass of molecule and M = mass of ion.

Let us then calculate the ratio of the mobility of a charged foreign ion in oxygen to that of an oxygen ion in oxygen on the (arbitrary) assumption that an ion is a charged molecule of the gas in which it was originally formed. The following figures are obtained :—Hydrogen 2.82, ammonia 1.20, carbon dioxide 0.93, ether 0.85, chloroform 0.80, recoil atoms from ThD 0.76. Heavier ions give a ratio approaching the limit 0.71 when their mass is infinite. The figures are not materially altered by substituting air for oxygen.

Four independent investigations have been made by Rutherford‡, Franck§, Blanc||, and Wellisch¶, and the

* Communicated by the Authors.

† Langevin, *Ann. de Chim. et de Phys.* (8) v. p. 245 (1905).

‡ Rutherford, *Phil. Mag.* v. p. 95 (1903).

§ Franck, *Deut. Phys. Gesell.* v. p. 397 (1909).

|| Blanc, *Journ. de Phys.* vii. p. 825 (1908).

¶ Wellisch, *Proc. Roy. Soc.* lxxxii. p. 500 (1909).

conclusion has been reached that the ion acquires a mobility which is independent of the gas in which it was formed, and cannot be distinguished from an ion formed directly in the gas in which the measurements are made. Rutherford's experiment was carried out with the positively-charged recoil atoms from radium and thorium emanation. The conclusion was that their mobility lay between 1.0 for radium and between 1.17 and 1.7 for thorium emanation—that is to say, was of the same order of magnitude as air ions.

Franck used the recoil atoms from ThD. He found that the mobility of these carriers in air was 1.56 and in hydrogen 6.21. In both cases the values are higher than the mean values of other experimenters for ordinary positive ions in these gases, the difference in air being as much as 10 per cent. The fact that the value is greater and not smaller, as might have been expected for such heavy atoms, suggests that the accuracy of a method depending on the deposition of active material on a plate is not great. A second experiment by Franck and Meitner* by another method gave limits to the mobility of these carriers in air, namely >0.7 and <1.6 †.

The experiments of Blanc were made by filling a dish with CO_2 , ionizing it with radium, and drawing ions of the appropriate sign into the air-space above and measuring their mobility by the Rutherford alternating field method. The experiment was then repeated without CO_2 , and it was found that the curves obtained in the two cases were in good agreement. But the experiment takes time, and the objection may therefore be raised that owing to convection and diffusion the CO_2 may have disappeared from the dish, and that consequently mainly air ions were being experimented upon in both cases.

The experiments of Wellisch are much more conclusive. Apart from showing that a mixture of gases such as oxygen and sulphur dioxide, or of ethyl ether and air, gave ions of a single value of mobility and not two values (in itself a very significant result), Wellisch carried out the following experiment. He took methyl iodide, which is strongly ionized by X-rays at 6 mm. pressure, filled up the vessel

* Franck & Meitner, *Deut. Phys. Gesell.* xiii. p. 671 (1911).

† As this paper is being sent for publication, an abstract of a paper read by Erikson before the American Physical Society has appeared in the 'Physical Review' (June 1924). He claims to have discovered two groups of ions of Actinium B in air, of mobility 3.15 and 1.20 respectively. He used air-velocities of 2000 cm./sec.; and until full details appear, one cannot help feeling that results obtained with such high air-speeds (involving eddies) must be viewed with caution.

with hydrogen to atmospheric pressure, and made a measurement of mobility by a modification of Langevin's method. He argued, with reason, that this was virtually a determination of the mobility in hydrogen of ions produced by the action of X-rays on methyl iodide. His conclusions were the same as those of Blanc.

To sum up, the experiments of Wellisch, and probably also those of Franck, make it clear that differences of the order of magnitude which the above calculation gives for the ions they used did not exist. Wellisch in consequence adopted the idea of an ion as a single molecule with a transferable charge, though Franck pointed out the difficulty of this hypothesis in the case of positive recoil atoms.

An apparatus used by the writers* for another purpose being readily available and apparently likely to give comparative results of a high order of accuracy, it was felt that further tests of this type were worth making, particularly with a view to their extension to hydrogen, ammonia, or any other substance lighter than air. If, for instance, one adopts the alternative view that an ion is a cluster of molecules loosely held to an ionized molecule and shed and replaced by other molecules when it passes into another gas, then if a small difference in mobility could be observed in any particular case, it might throw some light on the problem of the size of a cluster. If, for instance, on Langevin's formula we compare the mobility in air of a charged hydrogen molecule with that of a chloroform molecule when each of them is loaded with, say, 6 molecules of air, we should expect a ratio of 1.03, which should be readily detectable.

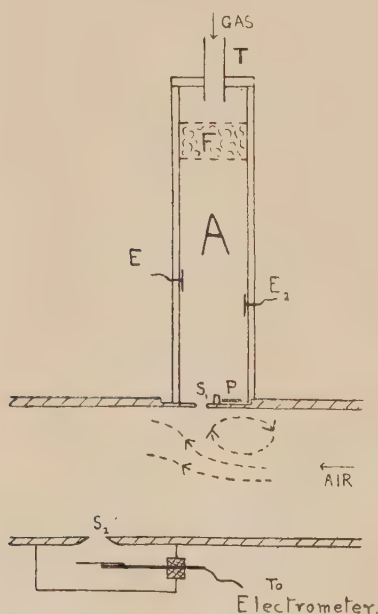
Briefly, the principle of this method was to produce the ions by polonium in a vessel A (fig. 1), to draw ions of one sign by an electric field through a slit S_1 into a long, shallow box through which filtered dry air was flowing, to drag them across the air-stream by another field, and to catch them on the other side of the box at another slit S_2 , which was adjustable in position relative to S_1 . Under given conditions the displacement of the ions downstream is a measure of their mobility. Owing, however, to diffusion the ions do not all travel along the same path, but reference to the original paper will show that the distribution curve at S_2 gives a well-defined peak from which measurements may be made. The method was slightly modified in the present work. Instead of keeping

* Tyndall & Grindley, *Phil. Mag.* April 1924.

the potential difference between the two sides of the box constant, and moving one slit relative to the other, the slits were kept fixed and the potential difference varied. It was found that this method gave somewhat sharper peaks than the earlier one.

The true position of the peak was estimated by taking several pairs of points symmetrically situated on a smooth curve through the observations, finding the mean voltage in each case, and averaging the results. The value obtained was in no case very different from that of the apparent peak of the smoothed graph.

Fig. 1.



Now, if the box A is filled with a particular gas, the ions will be formed in this gas, while their mobility measurement will be made in another—namely air. If previous experimenters are right in their conclusion that the measured mobility will be that of air ions and independent of the nature of the gas in which the ions were formed, then the position of the peak in the distribution curve at S_2

will be the same whether the vessel A is filled with air or with a foreign gas.

The vessel A was an airtight ebonite box (8 in. \times 2 in. \times 1 in.), into which the gas was introduced by means of a tube T. Some polonium, P, which ionized the gas above S₁, was so arranged that none of its α particles could pass through the slit. A layer of cottonwool F acted as a dust-filter, and ensured an approximately even flow of gas in the lower part of A. Two electrodes E₁ and E₂ (connected together) were arranged so that by applying a suitable potential to them a concentrated stream of ions could be directed to S₁.

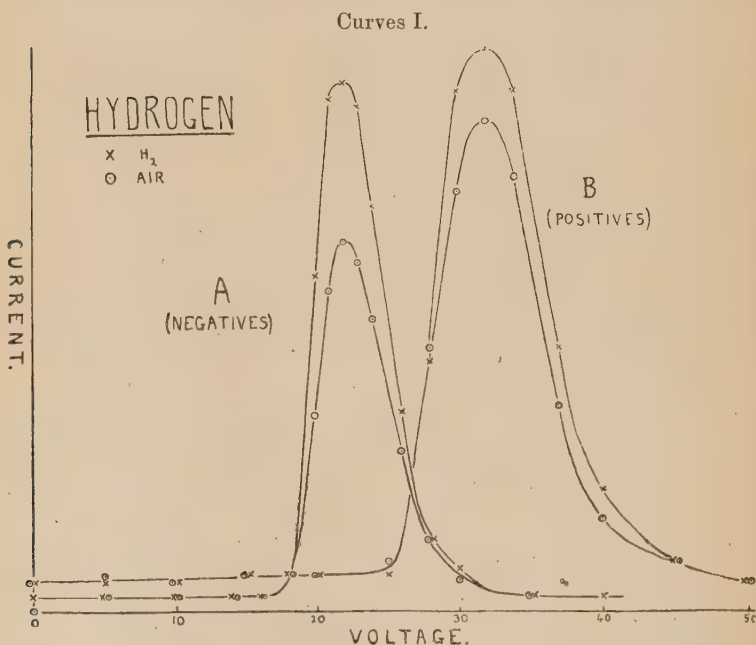
The method first adopted was to fill A by a rapid stream of gas through T, and then to cut A off from the supply while a reading of the electrometer was being taken. The peaks obtained in this way, however, were not identical in position with those due to normal air ions; but by mixing smoke with the air-stream through the box, the cause of this was shown to be eddy currents at the slit S₁ due to the difference in density between the two gases. Fig. 1, for instance, gives a rough indication of the eddy currents observed by smoke when the box A was placed above S₁ and was filled with hydrogen. It is clear from this that in the neighbourhood of S₁ there was an upward current tending to retard the motion of the ions across the box to S₂. Owing to this the apparent mobility would be too low; and this was exactly what the voltage curves indicated, the potential difference required to give the maximum current at S₂ being greater in the case of hydrogen than in the case of air. The effect was also found with coal-gas, and to a very slight extent with ammonia. The absence, however, of any second peak in the curves showed that the ions were homogenous.

In order to obtain a true mobility test, therefore, it was necessary to cut down the effect of these eddies as far as possible; and this was done by using a high velocity of air-current, by making the slit S₁ as narrow as possible (the width was cut down from 4 mm. to 2 mm.), and by taking the electrometer readings, when necessary, while a slow steady stream of the gas was being passed through T and S₁. Tests with smoke showed that under these conditions the disturbing upper eddy currents at the slit were (as far as one could see) eliminated.

The results obtained may be divided into two classes, according as the gas in A was (1) lighter, (2) heavier than air.

LIGHT GASES.

Hydrogen.—The hydrogen was prepared in a kipp from sulphuric acid and zinc, and passed through potassium permanganate and lead acetate solutions, pure sulphuric acid, and calcium chloride. The type of curve obtained is shown in Curves I. A and B, where the current received by the electrometer is plotted with voltage across the box. The crosses give the curves for ions produced in A filled with hydrogen, the circles for ions produced in A filled with air. Within the limits of experimental error the peaks for positive and



negative ions occur in each case at the same voltage, whichever gas supplied the ions originally. Taking a number of such graphs, the mean ratio of voltages—*i. e.* the ratio of mobilities—for hydrogen and air was 0.993 for positive and 1.006 for negative. This result is, however, not conclusive without further tests. It might be argued that owing to diffusion through S_1 the hydrogen was not pure, and that the density of ionization of the heavier air impurity in A was much greater than that of the hydrogen, thus giving a supply of ions which was mainly of air from the start. The results of drawing off samples of gas from A and

analysing them were not very conclusive, because air tended to be sucked into A through the slit S_1 in the process. The method referred to above of allowing a continuous slow stream of hydrogen to pass through A and out at S_1 served the double purpose of cutting down the eddy effect and improving the purity.

It is difficult to believe that under these circumstances the gas in A contained more than a small percentage of air. It might be argued even then that, despite their greater diffusion, hydrogen ions, owing to their higher mobility, will be trapped by the edges of the slit more readily than air ions, and that consequently relatively few of them will find their way into the air channel; but a subsidiary experiment with pure hydrogen above and below a slit showed that this was not the case. This being so, even if in the original experiment some air was present in A, there must have been an appreciable amount of hydrogen ions formed there which, had they retained their identity in the air-stream, would have given rise to a second peak somewhere in the curve. A careful test of the current supplied to S_3 was made over a wide range of voltage, without any suggestion of a second peak being found.

Finally, there was the possibility that the distortion of the field at S_2 due to the sharp edges gave rise to a similar sorting of ions of different mobilities, thus preventing hydrogen ions from reaching the electrometer. To show that this was not the case, a wire connected to the electrometer was inserted in S_2 flush with the surface, and on some occasions a potential of a volt or two was applied between it and the edges of the slit. Again, only one peak was observed, and this coincided with that appropriate to air ions.

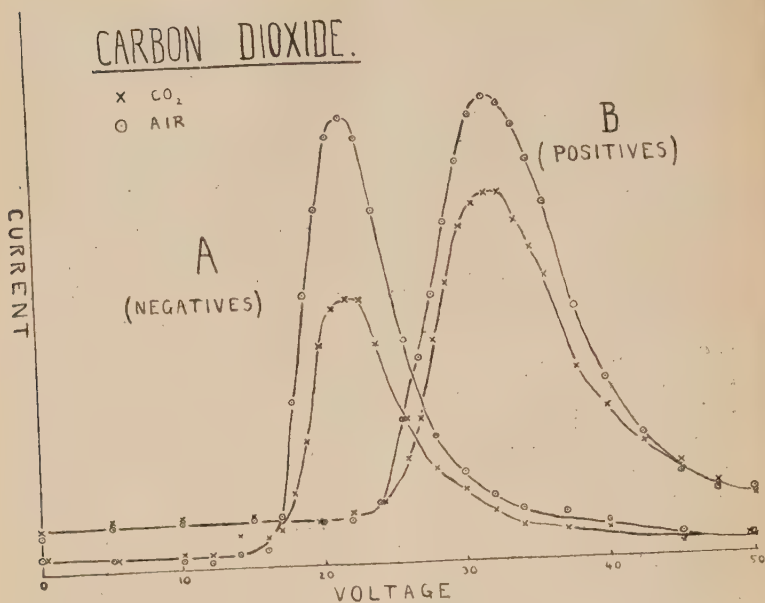
Ammonia.—The supply of ammonia was obtained by driving the air slowly through cotton-wool saturated in ammonia solution, and by placing in A cotton-wool soaked in ammonia solution. The graphs obtained were similar to those with hydrogen, the identity of the voltages at the peaks being shown by the following ratio for ammonia ion and air ion: positive ions = 0.991, negative ions = 1.003.

HEAVY GASES,

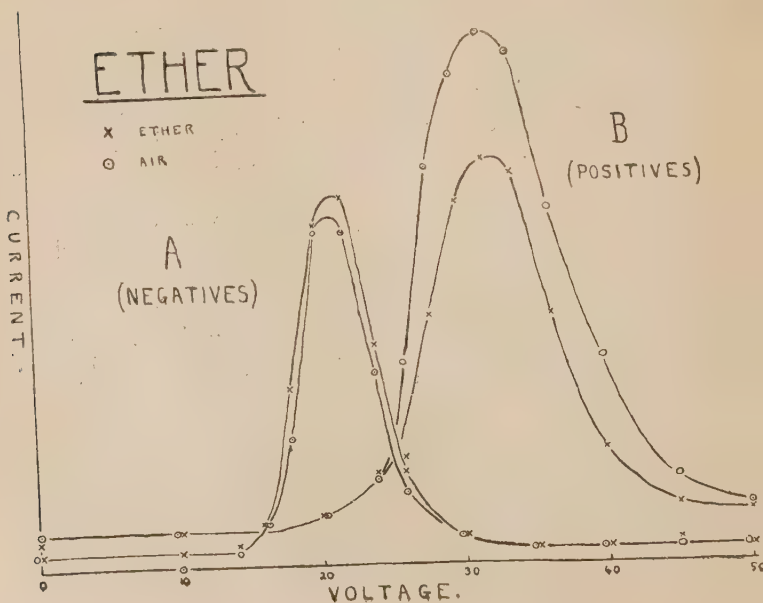
For this purpose the arrangement shown in fig. 1 was inverted, the chamber A being placed under the main mobility box.

Carbon dioxide.—The gas was prepared from marble and

Curves II.



Curves III.



hydrochloric acid and dried. The results are graphed in Curves II.; from such graphs the mean ratios for the voltages were: positive 1.001, negative 0.991.

Ether.—The air in A was saturated with ether by placing round its inner surface a layer of flannel soaked in ether. Curves III. show the graphs obtained, for which the ratios are: positive 1.004, negative 0.995.

Chloroform.—In this case liquid chloroform was placed in A. The ratios obtained were: positive 1.000, negative 1.006.

Incidentally, it may be pointed out that if all the results are grouped together, the value obtained for the ratio of the mobilities of negative and positive ions is very close to 1.50. This agrees more closely with the recent values of Loeb and of Wellisch than with earlier results.

Conclusions.

In all cases there is agreement in the position of the voltages at the peaks for air and the gas in question to under 1 per cent. That is to say, there is no sensible difference between the mobility of ions produced directly in air and that of ions produced in another gas or vapour and measured in air. This result agrees with the previous conclusion of Wellisch and others. But the agreement is probably more accurate, and moreover extends to other ionized gases and vapour, in particular to hydrogen and ammonia, which are lighter than air.

We are indebted to the Colston Research Society of the University of Bristol for assistance in the purchase of apparatus.

LXXIII. *The Distribution of Electrons among Atomic Levels.*
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1. Introduction.

THE scheme for the distribution of electrons among the completed sub-levels in atoms proposed by Bohr† is based on somewhat arbitrary arguments as to symmetry requirements; it is also incomplete in that all the sub-levels

* Communicated by R. H. Fowler, M.A.

† Bohr, *Zeit. f. Phys.* ix. p. 1 (1922); or 'The Theory of Spectra and Atomic Constitution,' Essay III. (Cambridge, 1922).

known to exist are not separately considered. It is here suggested that the number of electrons associated with a sub-level is connected with the inner quantum number characterizing it, such a connexion being strongly indicated by the term multiplicity observed for optical spectra. The distribution arrived at in this way necessitates no essential change in the process of atom-building pictured by Bohr; but the final result is somewhat different, in that a greater concentration of electrons in outer sub-groups is indicated, and the inner sub-groups are complete at an earlier stage. The available evidence as to the final distribution is discussed, and is not unfavourable to the scheme proposed.

2. Classification and number of X-ray Levels.

The X-ray atomic levels may be conveniently classified by means of three quantum numbers— n (total), k (azimuthal), and j (inner), as shown in Table I.

TABLE I.—Classification of X-ray Levels.

[“Relativity doublet” terms are bracketed.]

Level	K	L			M				
Sub-level		L_I	L_{II}	L_{III}	M_I	M_{II}	M_{III}	M_{IV}	M_V
n	1	2	2	2	3	3	3	3	3
k	1	1	2	2	1	2	2	3	3
j	1	1	1	2	1	1	2	2	3
Optical term ...	1σ	2σ	$2\pi_2$	$2\pi_1$	3σ	$3\pi_2$	$3\pi_1$	$3\delta_2$	$3\delta_1$

This classification has been put forward by Landé*. In contradistinction to the older schemes, such as that of Sommerfeld, it gives a satisfactory selection principle (k changes by 1, j by 1 or 0), and at the same time brings out clearly the analogy between X-ray and optical spectra. The sub-levels may, in fact, be regarded as corresponding to typical σ , π , δ ... doublet-series terms, as for alkali metal arc spectra, in the way indicated in the last row of the table.

The main criticism to be advanced against the classification

* *Zeit. f. Phys.* xvi. p. 391 (1922).

is that it invalidates the interpretation of terms such as $L_{II}-L_{III}$ as simple relativity doublets, although their separation is given accurately by Sommerfeld's formula. Bohr*, however, has shown that though L_I-L_{III} was to be regarded as a relativity + screening doublet, the further subdivision into separate relativity ($L_{II}-L_{III}$) and screening doublets (L_I-L_{II}) was not justifiable. De Broglie and Dauvillier†, who adopt a scheme somewhat similar to the above, but with a larger number of sub-groups, point out that the "relativity doublet" separation increases in a similar way to that of the optical doublet with increase in atomic number. Landé, in two recent papers‡, has traced out the analogy in quantitative detail. He shows that the relativity and optical doublet separations can both be represented by the same general formula, and places beyond doubt that the two types of doublet are essentially similar in origin.

Now, observations on the anomalous Zeeman effect show that the optical doublets must have a magnetic origin; and although the magnetic explanations are as yet inadequate, it is justifiable to apply those ideas which have coordinated the optical data to the case of X-rays—in particular in the assignment of inner quantum numbers, as in the above scheme.

De Broglie and Dauvillier postulate a larger number of sub-levels (6M, 10N ...) in order to account for certain weak X-ray lines observed; the necessity for this, however, is not admitted by most workers, and it is undoubted that not more than 5M absorption discontinuities have been directly observed§. The work of Robinson|| on excited electrons, moreover, seems to prove conclusively that there are only 5M, and probably 7N, levels. The experiments thus support the view that for Röntgen spectra, as for optical doublet series, the number of sub-levels characterized by different j 's into which a given k level subdivides is restricted to two.

* Bohr and Coster, *Zeit. f. Phys.* xii. p. 342 (1923).

† *Journ. de Phys.* VI. v. p. 1 (1924).

‡ *Zeit. f. Phys.* xxiv. p. 88 (1924) and xxv. p. 96 (1924).

§ Cf. Coster, *Phys. Rev.* xix. p. 20 (1922); Ross, *Phys. Rev.* xxii p. 221 (1923).

|| *Proc. Roy. Soc. civ.* p. 455 (1923).

3. *Suggested Distribution of Electrons.*

In the classification adopted, the remarkable feature emerges that the number of electrons in each completed level is equal to double the sum of the inner quantum numbers as assigned, there being in the K, L, M, N levels, when complete, 2, 8 ($2+2+4$), 18 ($2+2+4+4+6$), 32 ... electrons. It is suggested that the number of electrons associated with each sub-level separately is also equal to double the inner quantum number. The justification for this is discussed below. A summarized periodic table (Table II.) is given, which shows the nature of the distribution suggested. In the table the number of electrons in the sub-levels of the atom named on the left is given by the whole of the part of the table above and to the left of the thick line which begins under the atom. Krypton, for example, has 2K, 8L, 18M, and 8N electrons.

TABLE II.—Suggested Distribution of Electrons.

[The distribution of electrons in the atoms is given by the part of the table above and to the left of the thick lines]

Element.	Atomic Number.	Level (n).	Sub-Level, (k, j)						
			I	II	III	IV	V	VI	VII
			1, 1	2, 1	2, 2	3, 2	3, 3	4, 3	4, 4
He	2	K (1)	2						
Ne	10	L (2)	2	2	4				
A	18	M (3)	2	2	4	(4)	(6)		
Kr	36	N (4)	2	2	4	(4)	(6)	(6)	(8)
Xe	54	O (5)	2	2	4	(4)	(6)		
Nt	86	P (6)	2	2	4				

4. Comparison with Bohr's Distribution.

A summarized Bohr's periodic table (Table III.) is given for purposes of comparison. This, and also Table II., should be referred to in conjunction with a more complete table. The Bohr distribution cannot be easily put in the form of Table II., owing to the way in which the sub-groups undergo further development after reaching a first pseudo-completeness; but the relation between the two tables will be obvious on inspection.

TABLE III.—Distribution of Electrons in Atoms, according to Bohr.

Element.	Atomic Number.	Sub-Levels. (n, k .)									
		K	L		M			N			
		1	2	2	3	3	3	4	4	4	4
		1	1	2	1	2	3	1	2	3	4
.....	2	2									
.....	10	2	4	4							
.....	18	2	4	4	(4, 4)						
.....	36	2	4	4	(6, 6, 6)		(4, 4)				
.....	54	2	4	4	6	6	6	(6, 6, 6)		(4, 4)	
.....	86	2	4	4	6	6	6	(8, 8, 8, 8)		(6, 6, 6)	4 4

It can be seen at once that the distribution proposed is equally in harmony with the essential features of the development process pictured by Bohr as his own; which means that it is equally in accord with chemical considerations which are so beautifully covered by Bohr's scheme, especially in its attribution of the similarity in chemical properties of such sequences as the rare earths to the development of underlying groups of electrons.

A question which arises is whether the Bohr (n, k) levels are to be regarded as corresponding to the (n, k) or the (n, j) in the alternative scheme; for example, whether Bohr's (2, 1) level corresponds to L_I or $L_I + L_{II}$. The latter might seem reasonable in that (2, 2, 1) and (2, 1, 1) levels are more alike in certain respects, notably in energy

value, than $(2, 2, 1)$ and $(2, 2, 2)$; but the former is the direct and usual interpretation, and will be assumed here for the present. There is then a considerable difference in the assignment of electrons to (n, k) levels, the numbers running $(2, 6)$, $(2, 6, 10)$, and $(2, 6, 10, 14)$ for the L, M, and N (n, k) sub-groups in place of $(4, 4)$, $(6, 6, 6)$, and $(8, 8, 8, 8)$. If, however, Bohr's (n, k) , for this purpose, should be taken to correspond with our (n, j) levels, the numbers to be compared with Bohr's are $(4, 4)$, $(4, 8, 6)$, and $(4, 8, 12, 8)$.

As to the process of up-building, analogous sequences of elements correspond exactly on both schemes to analogous developments in the number and distribution of electrons; but the reorganization of underlying groups occurs in a much simpler manner in the scheme proposed. Beginning at Sc (21), 10 electrons complete the M group (noticeably beginning when there are 2, not 4, electrons in the N group); on our view these simply fill up the vacant $(n 3, k 3)$ levels, precisely 10 electrons being required; on Bohr's view the change also involves addition of electrons to the inner sub-levels—in fact, a complete reorganization of the whole M group. The added electrons referred to are bracketed in Table II., and the corresponding development on Bohr's scheme is indicated by the arrow in Table III. A similar process, probably beginning at Y (39), occurs when the 10 $(n 4, k 3)$ electrons are added, and again, beginning at Lu (71), for the 10 $(n 5, k 3)$ electrons. The $(n 4, k 4)$ level requires 14 electrons, and the adding of these corresponds to the rare earth sequence; on the Bohr view, a complete reorganization of the M group occurs. The dotted brackets and dotted arrow indicate this development.

The present scheme, then, accounts well for the chemical properties; it differs from Bohr's in the final distributions suggested, and in the fact that inner sub-groups are completed at an earlier stage, subsequent changes being made by simple addition of electrons to outer sub-levels without reorganization of the group as a whole.

5. Significance of Inner Quantum Numbers.

From a physical point of view, the real significance of inner quantum numbers, especially when applied to inner X-ray atomic levels, is very problematical. Evidence based on the analogous optical spectra, however, provides strong justification for the idea of the number of electrons

in a sub-group being related to the inner quantum number in the way assumed.

The case of the doublet series of the alkali methods only need be considered. In the atoms there is one electron external to a core composed of a completed system of electronic groups. Observations on the Zeeman effect can be correlated by assigning inner quantum numbers k and $(k-1)$ to the atom with the electron in a k level. For π terms ($k=2$), $j=1$ or 2 , giving π_2 and π_1 ; for δ terms ($k=3$), $j=2$ or 3 . There is actually a certain degree of arbitrariness as to the absolute value given to j ; for instance, values $\frac{1}{2}$ and $\frac{3}{2}$ for π_2 and π_1 , $\frac{3}{2}$ and $\frac{5}{2}$ for δ_2 and δ_1 can be made to fit the facts equally well*. This difficulty, however, is irrelevant, for the reason given below. The inner quantum number is usually interpreted as giving the magnetic moment of the atom as a whole, and the number of possible energy states of the atom in a weak external magnetic field, in which core and light electron are not separately affected, is attributed to the number of possible orientations of the atom in virtue of space-quantization.

The actual number of possibilities is given by the multiplicity of terms in the anomalous Zeeman effect, and can be deduced very straightforwardly (in simple cases at least) from observations on the behaviour of the lines. The point which it is desired to emphasize here is that, however the inner quantum numbers are interpreted, if they are given the values used above (k and $k-1$), twice the inner quantum number does give the observed term multiplicity as revealed by the spectra in a weak magnetic field. (Thus in a weak magnetic field there are 2σ , $2\pi_2$, and $4\pi_1$ terms.) In other words, the number of possible states of the (core + electron) system is equal to twice the inner quantum number, these $2j$ states being always possible and equally probable, but only manifesting themselves separately in the presence of the external field.

At present it is not clear whether the number of equally probable states indicates that the atom as a whole is always the same as concerns relative orientation of core and outer electron orbit, and can take up $2j$ different orientations relative to the (weak) field; or that the core takes up a definite orientation relative to the field, and the outer electron orbit can take up $2j$ different orientations relative

* For a fuller discussion of this whole subject, see Sommerfeld, 'Atombau und Spektrallinien,' and recent papers by Sommerfeld and Landé, *e.g.* Sommerfeld, *Ann. der Phys.* lxx. p. 32 (1923), lxxiii. p. 39 (1924); Landé, *Zeit. f. Phys.* xix. p. 112 (1921).

to the core*. (The mutual influence becomes of less relative importance as the strength of the field increases, so that ultimately the field affects electron and core separately, and the Paschen-Back effect is obtained.) There may be some quite different interpretation.

The spectral term-values themselves, in so far as they are altered by external fields, would seem to depend primarily on the outer electron orbit itself (and not so much on electron + core, as do the magnetic properties of the atom); and remembering this, it seems reasonable to take $2j$ as the number of possible equally probable orbits.

Without laying too much stress on any definite physical interpretation, or pressing the analogy too far, it may be suggested that for an inner sub-level, in a similar way, the number of possible orbits is equal to twice the inner quantum number, these orbits differing in their orientation relative to the atom as a whole. Electrons can enter a group until all the possible orbits are occupied, when the atom will possess a symmetrical structure.

That the inner quantum numbers are analogous to those for the alkali metals, is presumably connected with the fact that the building-up can always be regarded as occurring on a sub-structure of the inert gas atom type with completed group systems. The complicated optical multiplet series occur when there are light-electrons moving externally to incompleting groups.

In brief, then, it is suggested that, corresponding roughly to the definite indication in the optical case, the number of possible states of the atom is equal to $2j$; so, for the X-ray sub-levels, $2j$ gives the number of possible orbits differing in orientation relative to the atom as a whole; and that electrons can enter a sub-level until all the orbits are occupied.

6. Statistical Weight of Electrons bound in Atoms.

If electrons in the atom are distributed according to the present scheme, the interesting point is suggested that all electrons bound in the atom forming constituents of completed groups are to be regarded as having the same statistical weight, namely unity (or h^3); for there is then one electron in each possible equally probable state.

* This general question and the allied one of the orientation of the inert gas atoms in a magnetic field are discussed by Bohr, *Ann. der Phys.* lxxi. p. 228 (1923).

7. Evidence as to Electron Distribution.

Unfortunately there are few properties which depend solely on the number of electrons in levels and not also on the type of level and its energy value; so that, in the present state of theory, a definite test of the merits of different distributions proposed is difficult. Some evidence, however, is available from which a few conclusions may be drawn; and the general lines of evidence on which the question must finally be decided are briefly considered.

(a) Intensities of X-ray lines.

The intensity of X-ray lines will depend in part on the number of electrons in levels between which transitions occur; a simple relation between the relative numbers of electrons in two sub-levels and the relative intensities of the lines corresponding to transitions from these to the same final level would only be expected to hold when the sub-levels are close together, so that the energy associated with each transition is approximately the same, and when the sub-levels are of the same nk type. It has been shown for optical multiplets that the probability of possible transitions is not then dependent on the inner quantum number characterizing the terms concerned*. In the optical case, however, the outer electron switches over to a lower level, and no disturbing factors enter owing to the presence of intervening electrons between the levels concerned. For the X-ray case, on the other hand, transitions occur between levels across intervening occupied electronic orbits, which may modify the probability of transition from different j types of k orbit.—Simple relations would only be expected for transitions between contiguous levels such as $L \rightarrow K$, $M \rightarrow L$. A straightforward theoretical interpretation of observed relative intensities is thus only possible for a few cases.

From an experimental point of view, the relative intensity of different X-ray lines is difficult to determine, except when the lines are fairly close, so that corrections otherwise necessary, which cannot at present be accurately calculated, need not be applied. In one case very accurate measurements have been made, namely for $K\alpha_1 (L_{III} \rightarrow K)$ and $K\alpha_2 (L_{II} \rightarrow K)$. The results are as follows:—

	Fe.	Cu.	Zn.	Mo.	W.
α_2/α_1	·499	·512	·500	·52	·50

* Ornstein and Burger, *Zeit. f. Phys.* xxiv. p. 41 (1924).

The first three, due to Siegbahn and Žáček*, are the means of a large number of photometric measurements, agreeing closely among themselves; the last two, obtained from ionization measurements, are due to Duane and Patterson, and Duane and Stenström.

The ratio α_1/α_2 is thus practically constant and equal to 2/1 from Fe (26) to W (74).

This result can at once be explained on the assumption that there are twice as many electrons in the L_{III} as in the L_{II} sub-level. Now, in Bohr's scheme four electrons are assigned to the (2, 2) level, so that 4 electrons have to be divided between L_{II} and L_{III} —a ratio 3/1 or 1/1 for the α lines would be expected, certainly not 2/1.

For the $L\beta$ group, Duane and Patterson† give for tungsten $\beta_1, \beta_2, \beta_3, \beta_4$ as 100, 55, 15, 9. (See Table IV. for the transitions involved.) The β_3/β_4 value again suggests the 2/1 ratio for the number of electrons assigned to the M_{III} and M_{II} sub-levels. $\gamma_1, \gamma_2, \gamma_3, \gamma_4$ have relative intensities 100, 14, 18, 6. γ_2 and γ_3 correspond to transitions from N to L across the M group, and disturbing factors may come in, so that the γ_3/γ_2 value is not inconsistent with a 2/1 electron ratio.

The importance of disturbances due to intervening electrons must be stressed; for it should be noted that the relative intensities of components of doublets such as $\beta_3\beta_4$ and $\gamma_2\gamma_3$ change considerably with the atomic number, even after all the levels directly concerned are completed, the two components approaching equality for high atomic numbers.

As to switches from the same initial level to different final L levels, Coster‡ states that "for all elements l is 2–3 times as strong as η , and β_6 2–3 times as strong as γ_5 ," supporting the conclusion that L_{III} has twice as many electrons as L_{II} (so that it is twice as likely to lose an electron by ionization).

The very meagre results available as to line-intensities are practically exhausted in the above account; much further experimental (and theoretical) work is necessary. The results, however, do give definite support to the allocation of 2 electrons to the II sub-levels, and 4 to the III sub-levels, in the L, M, and probably N groups.

* Data used, together with references to the original papers, will be found in Siegbahn, 'Spektroskopie der Röntgenstrahlen' (Berlin, 1924), pp. 96, 97, 106.

† Proc. Nat. Acad. Sci. vi. p. 518 (1920).

‡ Phil. Mag. xliii. p. 1088 (1922).

TABLE IV.—Showing Transitions corresponding to K and L lines.

Level (<i>n</i>)	K(1)	L(2)			M(3)					N(4)				
Sub-level		I	II	III	I	II	III	IV	V	I	II	III	IV	V
<i>k, j</i>	1, 1	1, 1	2, 1	2, 2	1, 1	2, 1	2, 2	3, 2	3, 3	1, 1	2, 1	2, 2	3, 2	3, 3
Number of Electrons...	2	2	2	4	2	2	4	4	6	2	2	4	4	6
K Series	K	α_2 α_1			β_3 β_1					β_2				
L Series ... {	L_I				β_4 β_3					γ_2 γ_3				
	L_{II}				η β_1					γ_2 γ_3				
	L_{III}				l α_2 α_1					β_3 β_2				

Two other matters concerned with X-ray lines may be briefly noticed. Firstly, new lines would be expected to appear for the same atomic number on both Bohr's and the present scheme, as they are exactly similar as regards points of origin of group development. Secondly, if the appearance of "anomalous" longer wave-length satellites to lines is connected with the development of the corresponding, or associated, sub-groups, it might be possible to decide whether development occurs simply by addition of electrons to outer sub-groups, or also by reorganization of inner sub-groups. Coster gives some examples, but the data are insufficient as yet to make further discussion useful; it may be mentioned, however, that no irregularities are observed at all for β_6 and γ_5 during the development of the N group.

(b) *Absorption of X-rays.*

The relative absorption of X-rays by different sub-groups of electrons, as the relative intensities of lines corresponding to switches from them, will depend in part on the number of electrons they contain. Theories of absorption, as yet very incomplete, indicate that the part α_P of the characteristic atomic absorption due to a level P containing N_P electrons may be written :

$$\alpha_P = K\lambda^3 \frac{N_P}{f(n_P)},$$

where N_P is the corresponding total quantum number.

Kramers* does not consider the relative absorption for different subgroups (*e.g.* L_I , L_{II} , L_{III}), but gives as an approximate expression for the groups as wholes :

$$\alpha_P = K_1\lambda^3 \frac{N_P}{a_P n_P^3},$$

where a_P is the statistical weight of the electrons in the group. De Broglie†, semi-empirically, derives the expression :

$$\alpha_P = K_2\lambda^3 \frac{N_P}{\lambda_P^2},$$

λ_P being the critical wave-length for the level concerned.

* Kramers, *Phil. Mag.* xliv. p. 836 (1923).

† De Broglie, *Journ. de Phys.* VI. iii. p. 33 (1922).

As far as measurements on the relative K and L absorptions go, there is little to choose between the formulæ, though neither is adequate.

For orbits of a similar type, not too widely separated, it may, however, be anticipated that relative absorption, like relative emission, will depend primarily on relative numbers of electrons.

Owing to experimental difficulties, data as to relative absorption by different subgroups are meagre, Dauvillier's for gold being the only direct ones available *. From his curves based on ionization measurements on absorption in the L region of Au, he deduces for the relative absorptions, for $\lambda = \lambda_{L_I}$:

$$(M + N + O \dots) : L_{III} : L_{II} : L_I = 42 : 62 : 41 : 35,$$

and applying de Broglie's expression, obtains

$$N_{L_{II}}/N_{L_{III}} = .495, \quad N_{L_I}/N_{L_{II}} = .78,$$

a conclusion which may be taken to support the 2, 2; 4 distribution of electrons.

In the M region, photographic methods only have been used. All that can be said is that the greater contrast corresponding to transitions from the outer sub-levels (see, for example, the photographs of Ross † for Th) suggests that they contain a greater number of electrons, as in the 2, 2, 4, 4, 6 distribution proposed.

The most powerful method of investigating the relative absorption by different subgroups, however, is by investigating the secondary corpuscular rays ejected from them, as in the work of Robinson ‡. Using homogeneous X-rays, the electrons emitted from a secondary radiator are bent round in a magnetic field, and fall on a photographic plate. The relative intensities of the lines (really heads of bands) corresponding to electrons from the different levels, when these are fairly close, give a rough estimate of the actual relative numbers of electrons ejected. Using copper K α -rays, Robinson gives the following visually estimated intensities (on a 1-6 scale) for the lines corresponding to

* Dauvillier, *Comptes Rendus*, clxxviii. p. 476 (1924).

† Ross, *Phys. Rev.* xxii. p. 221 (1923).

‡ Robinson, *Proc. Roy. Soc. civ.* p. 455 (1923).

electrons ejected from the L sub-levels :—

	Ba.	I.	Sn.	Ag.	Mo.	Sr.	Cu.
L _I	1	2	2	3	3	5	5
L _{II}	1	3	3	4	4	5	5
L _{III}	6	6	5	5	5	5	

The remarkable fact appears that the relative absorption by the different sub-levels varies with the difference between the critical wave-lengths and the incident wave-length in a manner quite unforeseen by any theories hitherto put forward. This is also observed by Ellis and Skinner* with γ -rays. Over a wide range, however, in which the frequency is not too widely removed from the critical frequencies, and these themselves are not too close together, the run of intensities is exactly of the kind to be expected from a 2, 2, 4 distribution of electrons in the L subgroups; and in view of the strong evidence in favour of this distribution from other sources, it seems justifiable to consider the M intensities in a similar manner in the light of this. Robinson gives the following estimates :—

	Bi.	Pb.	Au.	W.	Ba.	I.	Sn.	Ag.
M _I	1	1	1	1	4	5	4	5
M _{II}	2	2	2	2	6	6	5	6
M _{III}	5	5	5	5	6			
M _{IV}	6	5	6	6	5	5	3	2
M _V	6	6	6	6				

Here, again, the general run of the figures in the range in which, from the L results, anomalies would be least expected, is in accord with the 2, 2, 4, 4, 6 distribution. (The M_I, M_{II}, M_{III} intensities show progressive change of the same type as the L_I, L_{II}, L_{III}, as would be anticipated from their respective k_j values being the same.) The N sub-levels of bismuth give :

	N _I .	N _{II} .	N _{III} .	N _{IV} .	N _V .	N _{VI} .	N _{VII} .
Bi	2	3	4	4	5	3-4	

Too much stress must not be placed on the evidence here brought forward as favouring the distribution proposed.

* Ellis and Skinner, Proc. Roy. Soc. cv. p. 186 (1924).

The estimate of intensities is arbitrary, and it is difficult to say how far the estimated values correspond to actual numbers of ejected electrons*. It has scarcely been sufficiently emphasized that the lines are really heads of bands; the number of electrons required is the total number in the band, and this number may diverge widely from that suggested by the line-intensity, particularly if the heads are close together. The inadequacy of theories of absorption, moreover, comes out most strongly in the very experimental results being considered. If, however, for sub-groups of similar energy relative absorption does depend largely on relative numbers of electrons under comparable conditions of excitation—and unless disturbing factors enter, it is difficult, physically, to imagine an alternative to this,—then the Robinson results do point definitely to a concentration of electrons in the outer sub-levels to an extent greater than it seems possible to account for on the basis of the Bohr numbers.

(c) *Magnetic Properties.*

The ionic paramagnetism of the third-period elements only will be briefly considered here. The development of ions from K_+ or Ca_{++} (with 18 electrons) to Cu_+ (with 28 electrons) is brought about, on our view, by the simple addition of electrons to the M_{IV} and M_V sub-levels in 10 (4+6) orbits of the same nk type (3, 3).

Sommerfeld, taking into account spatial quantization, has shown† that the number of Bohr magnetons associated with the ions increases regularly by steps of 1 from 0 to 5 (attaining this maximum value for Mn_{++} and Fe_{+++} with 23 electrons), and then decreases regularly to 0 (for Cu_+) with increasing numbers of electrons.

While the deeper meaning of this may be obscure, especially in that unit magnetic moment has apparently to be associated with (3, 3) orbits, such a beautiful regularity is in agreement with the development of the M group by the simple addition of 10 similar (n, k) orbits; the presence of x electrons in the (M_{IV} and M_V) levels, superposed on completed groups, may be expected (by a sort of Babinet principle!) to produce the same paramagnetic properties as (10— x) electrons, for with the latter number the group diverges from non-paramagnetic completeness in the absence of x electrons. On the Bohr scheme, the

* Robinson discusses this question, *l. c.* p. 473.

† Sommerfeld, *Zeit. f. Phys.* xix. p. 221 (1923).

development occurs by a complete reorganization of the whole M group from a (4, 4) to a (6, 6, 6) arrangement. While the general nature of the change might be the same, the essential and striking feature—the regularity—would certainly not be anticipated.

(d) *Chemical Properties.*

Chemical properties depend mainly on the number of electrons in outer I, II, III sub-groups. The distribution proposed is primarily concerned with completed groups rather than their course of development; but a few rather suggestive features of the new scheme, where it diverges from Bohr's, may be mentioned. The course of development strongly indicated for the L (Li-Ne), M (Na-A), N (Cu-Kr), O (Ag-Xe), P (Au-Nt) sub-groups is shown in Table V.

TABLE V.—Number of Electrons in Outer Sub-groups.

Outer Sub-Group.	Column of Periodic Table and Typical Element.							
	I	II	III	IV	V	VI	VII	VIII
	Na	Mg	Al	Si	P	S	Cl	A
I	1	2	2	2	2	2	2	2
II			1	2	2	2	2	2
III					1	2	3	4

A consideration of the electrovalency of the elements as indicated by the halides, for example, provides considerable evidence for a subdivision of electrons among the levels in this way. Thus P is 5-valent, corresponding to all the five outer electrons in PCl_5 , but also trivalent in PCl_3 corresponding to the three more loosely-bound ($M_{II} + M_{III}$) electrons. (Similarly, the analogous Sb.) S forms SF_6 , SCl_4 , and SCl_2 . (There are analogous Se and Te compounds.) Si and the analogues C, Ge, Sn, Pb all form tetrachlorides, and Sn and Pb dichlorides. I forms ICl_3 and IF_5 , and also compounds in which it acts as heptavalent.

The development of underlying groups occurring from Sc-Ni, Y-Pd, and Lu-Pt involves the addition of 4 and 6 electrons in IV and V sub-groups. (See Table III.) The problem of coordination compounds and "residual affinity" is undoubtedly linked up with these underlying groups, and in this connexion the prevalence of 6 as the number of groups surrounding the central atom in the ion of many complex compounds seems very significant as indicating 6 as the number of electrons to be associated with the outermost of the underlying sub-groups (V) when completed. As examples may be given the cyanides such as $H_4[Fe(CN)_6]$, $H_4[Ru(CN)_6]$, $H_4[Os(CN)_6]$, and the amines such as $[Co(NH_3)_6]Cl_3$, $[Pt(NH_3)_6]Cl_4$. The number 6 also occurs in the Bohr scheme in a somewhat similar manner, and the chemical evidence has already been discussed in this connexion*.

It seems undesirable here to enter more fully into chemical considerations, though they raise many important questions. The evidence is favourable, and the scheme seems to possess some new inherent possibilities for coordinating chemical facts.

A final remark may be made on the question of atomic symmetry as exemplified in carbon. According to Bohr, carbon has 4 (2, 1) electrons, whose orbits are taken to be tetrahedrally arranged. On the present view there are 2 (2, 1) and 2 (2, 2) electrons. The tetrahedral symmetry, therefore, is probably not to be attributed to the four outer electrons the atom possesses, but to the four "vacant places" which would have to be filled up for it to attain a complete configuration. Somewhat similar considerations may apply to the six-fold symmetry characteristic of coordination compounds of the type referred to above.

(e) *Optical Spectra.*

The relation between optical spectra and distribution of outer electrons has been (and is being) very fully considered by Bohr himself and others. Here it is only necessary to note the relevant fact that the doublet spectrum of ionized carbon (C II) † can at once be explained if C^+ has 2 (2, 1) electrons and 1 (2, 2); whereas it cannot be fitted easily into a 4 (2, 1) scheme for neutral carbon. The spectra of silicon in various stages of ionization fit in with the scheme proposed, as also the recently analysed oxygen spectrum ‡.

* Sidgwick, Journ. Chem. Soc. cxxiii. p. 725 (1923).

† Fowler, Proc. Roy. Soc. cv. p. 299 (1924).

‡ Hopfield, Phys. Rev. xxi. p. 710 (1923).

The correlation of the types of spectra with electronic structure, however, presents many unsolved problems for the future.

This section may be briefly summarized. The X-ray emission-line intensities seem to provide conclusive evidence for the presence of 2 and 4 electrons in L_{II} and L_{III} as inner atomic sub-levels over a wide range of atomic numbers, a subdivision also indicated for M_{II} and M_{III} . The absorption measurements confirm this, and suggest a distribution of the 2, 2, 4, 4, 6 type for the 5M and the first 5N sub-levels. The chemical evidence is strongly in support of the up-building of the I, II, III L, M, ... P sub-levels as suggested by the final 2, 2, 4 distribution, and this is confirmed in an important case by the optical spectra. The chemical properties also indicate strongly the number 6 as characterizing the M, N, and O V sub-groups, and magnetic considerations suggest 10 as the number of electrons in the completed M_{IV} and M_V sub-levels.

While evidence based on experiment is inadequate to provide quantitative proof of the correctness of the whole system of electronic distribution proposed, it seems conclusive as to the simpler sub-groupings, and collectively does lend strong support to a scheme in itself simple and consistent.

Summary.

A distribution of electrons in the atom is proposed, according to which the number in a sub-group is simply related to the inner quantum number characterizing it. A formal justification of the connexion is given. The suggested numbers of electrons in the sub-levels of the completed K, L, M ... groups are (2), (2, 2, 4), (2, 2, 4, 4, 6) ... respectively. The scheme is compared with that of Bohr. It enables all the essential features involved in Bohr's picture of atom-building to be retained, and so is equally in accord with general chemical and spectroscopic evidence; but it differs in the distribution in the completed groups, and in indicating a somewhat simpler mode of development. Evidence based on considerations of intensities of X-ray lines, absorption of X-rays, chemical and magnetic properties, and optical spectra is discussed and shown to give considerable support to a distribution of the kind put forward.

I would like to thank Mr. R. H. Fowler for helpful criticism and discussion.

Cavendish Laboratory,
July 1924.

LXXIV. *A Suggestion as to the Structure of Light.*

By Sir J. J. THOMSON, O.M.*

ONE of the most interesting facts in the history of the physical sciences is the contradiction between the evidence as to the nature of light afforded by its optical properties on the one side and its electrical ones on the other. There has perhaps never been a case where the agreement between the predictions of theory and the results of the most searching and accurate experiments has been so complete as in the undulatory theory of light—a theory which supposes that the disturbance which constitutes light is represented by a continuous function of the time and spatial coordinates and that the energy is distributed continuously throughout the beam. On the other hand, when we consider the electrical properties of light, everything points to great concentration of energy into discrete centres, and that “the front of a wave instead of being as it were uniformly illuminated is represented by a series of bright specks on a dark ground.”

Fig. 1.



Fig. 2.



Fig. 3.



Fig. 4.



The electrical properties point just as clearly to something resembling the Newtonian corpuscular theory as the optical ones do to the undulatory theory.

I have for a long time used a mental picture, based on the idea of tubes of electric force, which I have found useful in reconciling the optics with the electricity.

On this view the mutual potential energy of an electron E

* Communicated by the Author.

and a positive charge P is located in the tube of force stretching between E and P . If the electron falls from E to E' this potential energy is diminished by the energy in the portion EE' of this tube of force; for the energy in this portion to get free and travel out as light, the piece EE' of the tube must get into a state where it can travel freely with the velocity of light and not be associated with a charge of electricity whether positive or negative.

We may picture the energy as getting free in the following way : during the approach of E to P the tube EP may first be thrown into a loop as in fig. 2; the two sides of the loop near E' approach each other as in fig. 3; the closed part of the loop gets detached (fig. 4) and goes off as a closed ring, which rapidly becomes circular and travels with the velocity of light in a direction at right angles to its plane, like a circular vortex ring. The energy in the ring, which is that due to the fall from E to E' , remains constant as long

Fig. 5.

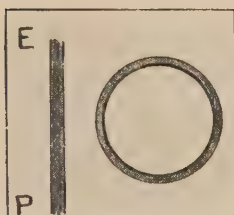


Fig. 6.

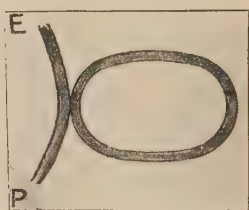


Fig. 7.

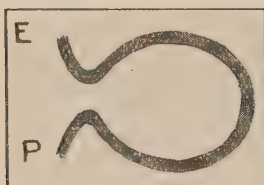


Fig. 8.



as the ring is unbroken. The emission of this ring is taken to represent the emission of radiation, and the energy of the light is concentrated in this ring.

For this ring to give up its energy a process the reverse of that which led to its formation has to be gone through. When the ring comes near a tube of force joining an electron to a positive charge, the stages indicated in the figs. 5, 6, 7, and 8 are gone through. When in the reverse

process the ring breaks and its tube of force gets attached to the electron in the stage represented in fig. 7, the energy in the circuit between P and E introduced by the ring is available for pulling the electron further away from P. If this energy is large enough to detach the electron from P, a free electron is produced and the ring disappears.

This will also be the case if the energy, though not sufficient to detach the electron altogether from P, is large enough to bring it into another position of equilibrium. Thus, suppose the electron were one in the second shell of electrons counting from the outside, there would be a position of equilibrium in the outer layer, and the energy of the ring would be spent in moving the electron from the second shell to the first, the ring would be destroyed, and there would be an absorption of energy. After a time the electron would fall from the first shell to the second, and emit the characteristic radiation by the processes indicated in figs. 2, 3, and 4. If, however, the energy in the ring were not sufficient to move the electron into a new position of equilibrium, then, though the absorption of the ring would make the electron start away from P, the forces acting upon it would soon stop it, and the motion would be reversed and the tube retrace its steps; the ring would be re-formed and break away from the molecule against which it struck, and in this case there would be no absorption.

Thus we see that the death of a ring means either the birth of a high-speed electron or the emission of a unit of characteristic radiation. This is in exact accordance with the exceedingly interesting and suggestive result obtained by Barkla, that when a beam of Röntgen rays is wholly absorbed in a gas without the emission of characteristic radiation, the number of high-speed electrons produced is independent of the kind of gas and its physical condition.

The rings are the centres in which the energy of light or Röntgen rays is concentrated. Any transference of energy from light to matter involves the destruction of these rings; thus the amount of energy transferred from a beam of monochromatic light or homogeneous Röntgen radiation must be an integral multiple of a unit.

Energy of a Ring.

If f is the electric polarization in the ring, the energy E is given by the equation

$$\begin{aligned} E &= 2\pi \times f^2 \times (\text{volume of ring}) \\ &= 2\pi \times f^2 \times \omega \times 2\pi r, \end{aligned}$$

where ω is the cross-section of the ring and $2\pi r$ its circumference. As the tube of force came from an electron $f\omega = pe$, where e is the charge on an electron and p a number not greater than unity, p would be equal to unity if all the lines of force from the electron were done up into one bundle; it will have a smaller value if there are more bundles than one. Substituting this value for f and writing $\omega = \pi b^2$, where b is the radius of the cross-section of the ring, we find

$$E = 8\pi^2 p^2 e^2 \frac{r^2}{b^3} \frac{1}{2\pi r}.$$

Thus, if the rings are geometrically similar, their energy will be inversely proportional to their linear dimensions.

Waves round the Ring.

At the time the ring is emitted from the atom, and indeed for some time before and after, the electric field in the atom is changing rapidly. This change will produce vibrations in the ring and give rise to electrical waves, so that before and after the ejection of the ring, electric waves are coming out of the atom; as these, like the ring, travel with the velocity of light, the ring will be the centre of a system of electrical waves of the normal type, and predominant among these are those which have the same periodicity as the vibrations of the ring. The energy in these waves will be small compared with that in the ring, because the total loss of energy by the atom is not far from the difference between the potential energy of the electrons in the positions E and E' .

We pass on now to consider whether this conception of the structure of light affords material for explaining interference and analogous phenomena.

We begin by remarking that the direction of motion of a free tube of force is at right angles to both the electric and magnetic forces, so that the direction of motion of such tubes may be altered by external electric and magnetic fields. As the ring is such a tube, the direction along which it moves can be deflected by applying electric or magnetic forces.

We suppose that when the ring is moving freely at right angles to its plane, it is surrounded and has travelling with it a distribution of electric force corresponding to a system of electrical waves of the ordinary type, diverging from the atom or molecule from which the ring was emitted. The distribution of electric force is periodic, and the period is

a period of vibration of the core about its circular configuration. If the waves surrounding the ring fall on a narrow slit in a metal plate parallel to the plane of the ring, the electric and magnetic forces in the parts of the wave in the slit are much greater than they were before the wave reached the slit. The directions of these forces change as well as their intensities, so that the Poynting vector, *i. e.* the direction of the flow of energy, will change in direction from place to place in the neighbourhood of the slit. Thus the flow of energy gets diverted when the wave passes through the slit; it is no longer always in one direction, but spreads out fanwise after leaving the slit. The result of this spreading is shown by the ordinary theory of diffraction to lead to such a distribution of energy in the electrical waves after they have passed through the slit, that the density of energy travelling in a direction making an angle θ with the normal is proportional to $\sin^2 m\theta / (m\theta)^2$, where m is a constant depending on the wave-length of the light and the width of the slit. The energy-path for a particular piece of energy will depend upon the part of the slit through which that energy passes.

As the ring is a tube of force, its path will be affected by the changes produced by the slit in the electric and magnetic force in the waves enveloping the ring. Since the ring is closed, it will give rise to but very small external magnetic and electric force; thus at places on a surface surrounding the ring and but a little way from it the electric and magnetic forces, and therefore the Poynting vector, will not be affected by the presence of the ring. We shall suppose that the path of the energy of the ring is the same as the path of the energy in the wave in its immediate neighbourhood. The angle through which the path of the energy is deflected will depend upon the part of the slit through which the ring passes. As the dimensions of the ring will in general be very small compared with the width of the slit, the ring is as likely to pass through one part of the slit as another; hence when a very large number of these rings pass through the slit, the flow of energy will be uniform throughout the slit, and the energy sent in any direction θ will be proportional to that sent in the same direction by a plane continuous electric wave travelling horizontally towards the slit—*i. e.*, it will be proportional to $\sin^2 m\theta / (m\theta)^2$. Thus on these assumptions the diffraction patterns will be the same when the energy of the light is concentrated in a ring as when it is, as in the ordinary theory, spread throughout the whole of the wave. We can

apply the same considerations to explain the other interference effects, such as Fresnel's mirrors and the scattering of light and Röntgen rays by the molecules of a gas.

To sum up, light on this view is made up of units, each of which contains a core in which the energy is concentrated ; this core is surrounded by a system of electric waves which, though they have but little energy, give rise in cases where diffraction or interference occurs to electric and magnetic forces which deflect the paths of the cores without altering their energy. The core is supposed to vibrate in a definite period, and this period coincides with that of the electrical waves which surround it.

Planck's Law.

There ought on this law to be a very simple relation between the energy of the ring and the frequency of the light of which it is the unit. If E is the energy and ν the frequency,

$$E = h\nu$$

where h is Planck's constant 6.55×10^{-27} .

Thus the frequency of the light is directly, and the wave-length inversely, proportional to the energy. This kind of relation might be expected on the view we are discussing, for we have seen that the energy of the ring is equal to

$$8\pi^2 p^2 e^2 \frac{r^2}{b^2} \frac{1}{2\pi r} \dots \dots \dots (1)$$

If the rings are geometrically similar, r/b will be the same for all rings. The frequency of the waves is the same as that of the ring ; in geometrically similar rings we should expect the wave-length of the vibration to be proportional to the linear dimension. Hence from (1) we should expect the energy to be inversely proportional to the wave-length ; this is Planck's law. To estimate whether the value of the constant would be anything like Planck's value ; let us suppose that the time of vibration of the ring is the time taken by light to travel round the circumference of the core ; then $\nu = c/2\pi r$, where c is the velocity of light. Hence from (1)

$$E = 8\pi^2 p^2 e^2 \frac{r^2 \nu}{b^2 c} ;$$

$$e = 4.8 \times 10^{-10},$$

$$c = 3 \times 10^{10},$$

$$E = 6.2 \times 10^{-28} \frac{p^2 r^2}{b} \cdot \nu.$$

So that if $pr/b=\pi$, the numerical value of the constant connecting E and ν would agree well with Planck's value.

Absorption of Light.

Absorption of light on this view involves the rupture of the rings forming the cores; the endless ring has to be broken, and, as its end cannot be free, they must join on to another tube of force connecting electrons and positive charges, the energy in the ring being communicated to the carriers of those charges. We have seen that for the ring to be permanently destroyed, the energy in the ring must be sufficient to produce some quasi-permanent change in the molecule, such as the ejection of an electron, or the movement of an electron from one position of equilibrium to another; if no such change is possible, the substance cannot take any energy from the light, and so will be quite transparent. Apart from selective absorption and resonance, which requires special treatment, the transparency of many substances to light in the visible or infra-red spectrum is very high; thus, for example, the light that reaches us from the sun and stars has passed through matter equivalent in mass to a layer of mercury 30 inches thick. On the other hand, ultra-violet light of very small wave-length, as in Schumann rays, may be absorbed by a layer of gas a few millimetres thick at a low pressure, and this effect seems too general to be altogether selective. The energy in each unit of light of this character, say of wave-length 1000 Å, is that corresponding to about 12 volts, which is of the order of the ionizing potential of gases; thus units of light of this kind have enough energy to produce a very definite chemical change in the molecule, and so would be liable to be absorbed.

Several factors have to be taken into consideration with regard to absorption. First the energy in the unit. An increase in this may enable the unit to effect certain changes, such as the expulsion of an electron or the removal of an electron from one layer to another, and thus increase the absorption. When the energy in the unit is sufficient to produce all possible permanent or quasi-permanent changes in the disposition of the electron, any further increase in the energy is not likely to lead to an increase in the absorption. When the unit has enough energy to be absorbed, the amount of absorption will depend upon the number of electrons hit by the ring as it passes through the absorbing substance; this number will depend upon the size of the ring. Now, as we have seen, the radius of the ring is

inversely proportional to the energy, so that with an increase in energy the radius of the ring diminishes. Thus the effect of an increase in energy will be twofold ; it may increase the probability of a unit being absorbed if it makes a collision, but it diminishes the probability of the collision. When the energy in the ring is far greater than that corresponding to the ionizing potential of the gas, the second effect will be the more important, and the absorption will diminish as the size of the ring diminishes—*i.e.*, as the energy increases. On the other hand, when the energy in the ring sinks below that required for ionization complete or partial, the absorption will vanish ; hence at this stage there should be an enormous increase in absorption as the energy increases through a critical value—the absorption will reach a maximum and then diminish whether the energy increases or diminishes.

Knowing the dimensions of the ring, the distance it must travel before meeting with an electron can be calculated without difficulty. We must remember, however, that a ring may meet an electron without suffering disruption, for it is only when the tube of force attached to the electron has the proper orientation with respect to the core that the process indicated in figs. 5, 6, 7, and 8 can take place, so that it is only a small fraction of the number of collisions between the rings and electrons which lead to disruption and therefore to absorption.

From these principles we can calculate the coefficient of absorption of light ; for if $1/\lambda$ is the value of this coefficient, λ is the average distance travelled by a light-core before it is destroyed and its energy spent in increasing either the kinetic or potential energy of an electron. If A is the area of the cross-section of the light-core made by a plane through its centre and at right angles to the direction in which the ring is moving, and n the number per unit volume of electrons of the type of those which are to be detached or permanently displaced by the ring, the number of such electrons struck by the ring when it passes over a distance x is equal to Axn . In order that the electron should be detached, it is not sufficient for it to be struck by the ring ; it must be struck when the tube of force attached to the electron is directed so that the processes shown in figs. 5, 6, 7, and 8 can occur. This tube must point in a particular direction, or rather it must be included in a cone of small angle. If α is the semi-vertical angle of this cone, then if the orientation of the tube is not affected by the ring, the chance that the tube should point in the proper direction is $\sin^2 \frac{\alpha}{2}$. Thus, if

the ring were to move through a distance x , the number of times it would have met with an electron which would have broken it up is $xAn \sin^2 \frac{\alpha}{2}$; hence λ , the average distance a ring travels before being destroyed, is given by the equation

$$\lambda = \frac{1}{An \sin^2 \frac{\alpha}{2}},$$

and the chance of the ring travelling a distance x without being absorbed is $e^{-x/\lambda}$. The minimum value of λ is $1/An$ and the maximum value of the coefficient of absorption An . For the absorption to be as great as this, every electron when struck by the ring must have its tube of force pointing in the right direction: for this to be the case the direction of these tubes of force must be determined by the light wave itself.

Resonance.

The effect of resonance on this theory is due to the effect of the light on the orientation of the tubes of force attached to the electrons. Suppose that the period of the light is the same as that of the electron which is to absorb the energy of the ring; then the waves preceding the ring having the same period as this electron will have a great effect upon it and will make the tube of force attached to it tend to point in a definite direction. Thus, when the ring strikes the electron, the tube of force attached to the electron, instead of being as likely to point in one direction as in any other, will be concentrated along a definite direction, so that the probability of the rupture of the ring will not be the same as when there is no resonance. If the directions of the electron tubes were all brought by the resonance effect into the position for the rupture of the ring, the free path of the ring would be $1/An$ instead of $1/An \sin^2 \frac{\alpha}{2}$, and the coefficient of absorption would be An ; hence a slower limit to An would be the coefficient of absorption of the light. The only value for such a coefficient I have been able to find is one given by Professor R. W. Wood (Phil. Mag. xxiii. p. 696, 1912), who found that the intensity of the mercury line 2536 was reduced to half its value by passing through 5 mm. of mercury vapour at a pressure of 0.001 mm.

Hence, if a is the coefficient of absorption,

$$a = 2 \log_e 2 = 1.4.$$

The number of atoms of mercury in 1 c.c. at a pressure of .001 mm. at 0°C is 3.6×10^{13} .

The electrons concerned with light of this wave-length are those of the outer layer. We shall suppose that there are two such electrons per atom; hence $n = 7 \times 10^{13}$. The lower limit of A is given by the equation

$$\begin{aligned} An &= a & \text{or} \\ 7 \times 10^{13} A &= 1.4; \end{aligned}$$

hence the lower limit of A is 2×10^{-14} . This is considerably greater than the area of a circle whose radius is that of the atom; as the ring is an anchor-ring with a hole in the middle, the radius of the ring forming the core of light of this wave-length must be much larger than 10^{-8} . So that the rings for light of this quality must be large compared with atoms.

The mass of a ring is equal to $2h/c\lambda$, where h is Planck's constant 6.55×10^{-27} , c the velocity of light 3×10^{10} , and λ the wave-length. Even when the wave-length is as small as the radius of an atom, this mass is very small compared with that of an electron 8.8×10^{-28} ; so that in a collision between an electron and a ring there would be very little transference of energy, though the effect on the direction of motion of the ring might be considerable.

On the view we have taken, the production of a ring is due to a deformation in the tubes of electric force produced by a rapid diminution in the potential energy. It is possible to imagine electric waves without a ring; thus, if an electron is moved with uniform velocity round the circumference of a circle with a positive charge at its centre, electric waves whose frequency is that of the moving electron will be generated, but will not necessarily be accompanied by a ring.

LXXV. *On the Relation between Metal Contact Potentials and the Peltier Effect.* By J. A. V. BUTLER, M.Sc., University College of Swansea*.

THE electromotive force in a closed circuit of two metals A and B with junctions at the temperatures T_1 and T_2 may be expressed by either of the following equations:—

$$e = E_1 - E_2 + \int_{T_1}^{T_2} (\rho_a - \rho_b) dT, \quad \dots \dots (1)$$

$$e = q_1 - q_2 + \int_{T_1}^{T_2} (\sigma_a - \sigma_b) dT, \quad \dots \dots (2)$$

* Communicated by the Author.

where

e = e.m.f. of the whole circuit.

E_1, E_2 = contact P.D.'s at the junctions at T_1, T_2 respectively.

q_1, q_2 = corresponding reversible heat effects at the junctions. (Peltier coefficients.)

ρ_a, ρ_b = P.D.'s in the two metals A and B for unit difference of temperature.

σ_a, σ_b = corresponding Thomson coefficients, i.e., reversible heat effects in passage of unit quantity of electricity through unit difference of temperature.

The first equation expresses the fact that the e.m.f. round the circuit is the sum of the individual P.D.'s; the second is an expression of the first law of thermodynamics as applied to the thermoelectric circuit which demands that the heat absorbed in the Peltier and Thomson effects shall be equal to the Joulian heat evolution in the whole circuit, e per unit quantity of electricity. The similarity between (1) and (2) has led to their frequent identification term by term, and the confusion which has resulted has persisted in text-books and original papers to the present time.

Apart from this confusion of thought the numerical correspondence of E and q has been very strenuously maintained. Sir Oliver Lodge, at one time the champion of this view *, vigorously maintained that "The total contact force at any junction can be experimentally determined by measuring the reversible energy developed or absorbed there per unit quantity of electricity conveyed across the junction."

Now the reversible heat evolution at a junction is equivalent to a few millivolts at the most. Those who took the view that this was the whole electromotive force at the junction were bound to ascribe the much greater Volta potential to other effects, e.g., to "chemical action" in the system A/air/B †.

In more recent times overwhelming evidence has accumulated which makes it impossible to doubt the existence of a real contact difference of potential between two metals of a much greater order of magnitude than the Peltier effect. It is demanded by the theory of electron emission from metals ‡; it has been experimentally demonstrated in a

* Phil. Mag. [5] vol. xix. (1885); B. A. Reports, Montreal, 1884.

† Lodge, *loc. cit.*; also Phil. Mag. vol. xlix. p. 351 (1900), Proc. Phys. Soc. Lond. vol. xvii. p. 369 (1900).

‡ Cf. Richardson, 'Emission of Electrons from Hot Bodies.'

particularly conclusive and elegant manner, by Millikan and his co-workers*.

What, then, is the relation between the Peltier heat effect and a junction and the real contact P.D.?

We shall endeavour to give a fairly complete answer to this question by developing the statistical theory of metal boundary potentials, the results of which will be shown to be entirely in accordance with the requirements of the laws of thermodynamics.

It can be shown†, by means of a thermodynamical argument (and indeed is obvious if the matter is viewed rightly), that if w_a and w_b are the latent heats of evaporation of electrons from the two metals and therefore $w_a - w_b$ is the total energy change in the transfer of an electron from A to B, that

$$E - \frac{w_a - w_b}{F} = q, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now rewriting (1) and (2) in the differential forms

$$de = dE + (\rho_a - \rho_b)dT, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$de = dq + (\sigma_a - \sigma_b)dT, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and applying the second law of thermodynamics to the reversible heat effects by means of the equation

$$d(q/T) = - \frac{\sigma_a - \sigma_b}{T} dT,$$

we obtain the well-known Kelvin equation

$$q = T \frac{de}{dT}, \quad . \quad . \quad . \quad . \quad . \quad (5A)$$

and introducing this value of q into (3), we find

$$E - \frac{w_a - w_b}{F} = T \frac{de}{dT}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

an equation which resembles the well-known Gibbs-Helmoltz equation for the whole of a galvanic cell,

$$\epsilon - \frac{U}{nF} = T \frac{d\epsilon}{dT},$$

but differs in that in (6) e refers to the whole circuit whereas E refers only to one junction.

The relation between contact potentials and the Peltier

* Phys. Rev. vol. vii. p. 18 (1916); vol. xviii. p. 236 (1921).

† Richardson, 'Electron Theory of Matter,' 1916, p. 455.

effect has also been investigated by Lord Kelvin *, who made use of a very ingenious thermodynamical engine and obtained the equation

$$\frac{dV}{dt} = Q/t,$$

where V = Volta P.D. at junction.

Q = sum of Peltier effect at junction and "quasi-Peltier effects" if any at air or ether metal surfaces.

The matter cannot be pushed any further on these lines because it is not possible to treat thermodynamically the behaviour of a single junction, *i.e.*, without introducing a return path. In order to elucidate it further it is necessary to turn to statistical considerations.

Statistical Theory of Metal Boundary Potentials.

Case (a).—Consider a single metal in a closed space containing an electron atmosphere of concentration electrons per unit volume, all at the temperature T . The rate at which unit area of the metal loses electrons at this temperature when uncharged is given by the ordinary thermionic expression. The rate at which electrons are deposited from the atmosphere is $n\sqrt{T/2\pi m}$. If the rate of loss is greater than the gain, the metal will acquire a positive charge which will accumulate until a state of balance is reached. Let the surface P.D. corresponding to the work done against this charge by an electron in escaping be E . The work which an electron must do before escaping from the metal is now $W_1 - EF$ and the condition of equilibrium is

$$k_1\sqrt{T}e^{-\frac{w_1 + EF}{RT}} = n\sqrt{T/2\pi m}, \quad . \quad . \quad . \quad (7)$$

(assuming that the electron concentration is not markedly affected in attaining equilibrium) ;

$$\therefore E = -\frac{w_1}{F} - \frac{RT}{F} \log_e n - \frac{RT}{F} \log_e K. \quad . \quad . \quad (8)$$

The potential difference at the surface of a metal therefore depends on the concentration of the electron atmosphere and varies logarithmically with it.

Case (b).—Now consider the case of two metals in the electron atmosphere together but not in contact. Equilibrium at the surface of each will be conditioned as in Case (a) and equilibrium will be represented by the equations

$$k_1\sqrt{T}e^{-\frac{w_1 + E_1 F}{RT}} = n\sqrt{T/2\pi m},$$

$$k_2\sqrt{T}e^{-\frac{w_2 + E_2 F}{RT}} = n\sqrt{T/2\pi m},$$

* Collected Works, vol. v. p. 29; Phil. Mag. vol. xlvi. p. 82 (1898)..

whence
$$E_1 - E_2 = \frac{w_2 - w_1}{F} + \frac{RT}{F} \log_e \frac{k_1}{k_2} \quad (9)$$

That is, although the surface P.D. of both metals is dependent on the electron atmosphere concentration, the difference for any two metals is characteristic of them, therefore their intrinsic P.D.

Case (c).—We can now consider the case of two metals in contact. It can be said at once that the conditions at the surfaces not in contact are unaltered, that when equilibrium is attained electrons arrive at and escape from every portion of the metals at equal rates. Otherwise a continuous flow of electricity across the junction would be necessary to redress the balance, and a heat absorption or evolution at the junction by the Peltier effect would occur which would violate the second law of thermodynamics. There must therefore be a P.D. at the metal junction equal to the intrinsic P.D. of the metals, and at equilibrium equal numbers of electrons must pass the junction between the metals in both directions in the same time.

Before an electron can escape from either metal into the other, it will have to perform a certain amount of work. This may not be identical with the thermionic work function w_1 or w_2 ; the forces of attraction exerted on an electron by the metals on either side of the junction may overlap to some extent, but the work done against these forces in the transfer of an electron from the interior of the first to the interior of the second metal must always be $w_1 - w_2$. Let the amounts of work against these attractive forces to be done in escaping across the boundary from the metal on either hand be w_1' and w_2' . The rates of escape before any electric forces are set up will be $k_1 e^{-w_1'/RT}$ and $k_2 e^{-w_2'/RT}$. If these are unequal an accumulation of electrons on one side of the boundary will occur until the electric forces so set up effect a balance. Let the amounts of work to be done before passage across the boundary from either side be now $w_1'' + e_1 F$ and $w_2'' - e_2 F$ where $w_1'' - w_2'' = w_1 - w_2$ and $e_1 + e_2 = E$, the total P.D. between the metals. Then the condition of equilibrium is

$$k_1 \sqrt{T} e^{-\frac{w_1'' + e_1 F}{RT}} = k_2 \sqrt{T} e^{-\frac{w_2'' - e_2 F}{RT}} \quad (10)$$

Let
$$\frac{w_1 - w_2}{F} = U_0 \quad \text{and} \quad \frac{k_1}{k_2} = K.$$

Then
$$E = -U_0 + RT/F \log_e K. \quad (11)$$

Hence by comparison with (9) $E = E_1 - E_2$.

Now the heat absorbed in passing the junction is equal to

the total energy change U plus the work done in going up the potential difference E^* . Our expression for the Peltier coefficient q is therefore

$$q = E + U = \frac{RT}{F} \log_e K + \xi_2 - \xi_1. \quad (12)$$

Differentiating (11) and (12) we obtain

$$\begin{aligned} \frac{dE}{dT} &= \frac{R}{F} \log_e K = \frac{q_0}{T} \\ \frac{dq}{dT} &= \frac{dE}{dT} + (\sigma_2 - \sigma_1), \end{aligned}$$

since by Kirchhoff's equation the temperature coefficient of the total energy change at the junction must be equal to the difference between the specific heats of electrons in the two

metals, i. e., $\frac{dU}{dT} = \sigma_2 - \sigma_1$.

From (5) therefore

$$\frac{de}{dT} = \frac{dE}{dT} = q_0/T, \quad \dots \dots (13)$$

and to the first approximation,

$$\frac{d^2e}{dT^2} = \frac{\rho_2 - \rho_1}{T} \dagger \quad \dots \dots (14)$$

Now whereas the conception of the origin of the Peltier effect and the general form of its relation with the corresponding contact P.D.'s which has been developed is entirely in accordance and is a logical development of the whole body of the thermionic theory, quantitatively it depends on the validity of the fundamental thermionic equation. In particular the use of the equipartition value RT in the denominator of the exponent is open to criticism, and it is assumed without justification that k is independent of the temperature. It is quite possible, for example, that k is a function of the specific heat of electrons in the metal, in which case some modification of the thermoelectric equations would be required.

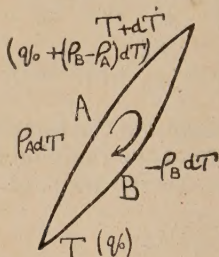
Under these limitations an interesting conclusion can be drawn from (13), which implies that the difference in the contact P.D.'s in thermoelectric circuit accounts for the whole of the e.m.f., i.e., that the Thomson effect in the closed circuit does not contribute to the e.m.f.

This conclusion, which at first sight appears somewhat

* $U = U_0 + \xi_2 - \xi_1$ where ξ_2 and ξ_1 are the thermal energies of electrons in the two metals. $q_0 = A + U_0$.

† This equation has recently been directly verified by Latimer. Journ. Amer. Chem. Soc. vol. xlv. p. 2136 (1922).

improbable, is made more understandable by the following considerations. In the passage of electrons round a closed circuit of two metals with junctions at different temperatures, the heat effect $\int(\rho_A - \rho_B)dT$ in the homogeneous conductors due to the heat capacity of electrons is balanced by differences in their thermal energy changes in crossing the two junctions. This is evident from the diagram. The resultant heat effect



is simply $dE = R \log_e K \cdot dt$. Hence (13) in no way violates the conservation of energy.

It by no means follows that there is no difference of potential along a homogeneous conductor in which there exists a temperature gradient, only that the P.D. must be the same in all conductors for the same temperature difference.

It must be observed that the equation $de/dT = q_0/T$ is similar but not identical with the thermodynamical equation (5 A). The difference may be due to the uncertainties in the thermionic equations referred to, but it must also be remembered that in the thermoelectric circuit the reversible effects are necessarily accompanied by certain irreversible phenomena, and as Richardson has recently pointed out*, "the assumption that the laws of thermodynamics as they apply to reversible cycles can be applied to reversible effects superposed on such a system is one which has never been proved to be necessarily valid."

Summary.

The statistical theory of metal boundary potentials is developed and an equation giving the relation between the thermionic work functions of metals and the corresponding contact P.D.'s is obtained. The Peltier heat effect at the junction of two metals is accounted for and the various equations of the thermoelectric effect in a circuit of two metals with junctions at different temperatures are completely co-ordinated. On certain assumptions these equations lead to the conclusion that the Thomson P.D. is the same for the same difference of temperature in all conductors.

* Proc. Roy. Soc. [A], vol. cv. p. 387 (1924).